PB83-127696

Analytical Methods for By-Products PCBs-Preliminary Validation and Interim Methods

Midwest Research Inst.
Kansas City, MO

Prepared for

Environmental Protection Agecny
Washington, DC

11 Oct 82

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Office of
Toxic Substances
Washington DC 20460

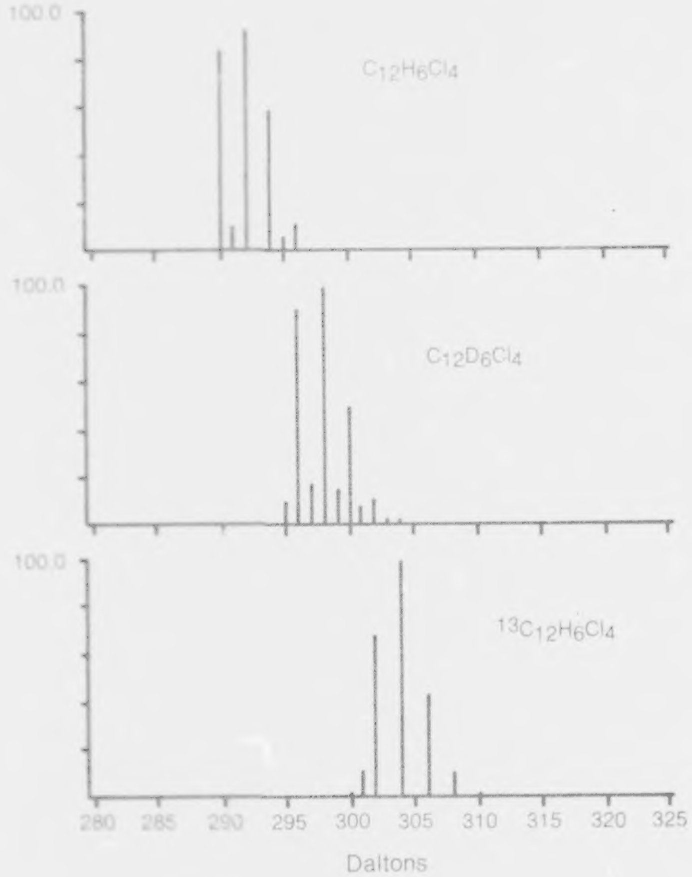
EPA-560/5-82-006
October, 1982

PB83-127696

Toxic Substances

EPA

Analytical Methods for By-Product PCBs— Preliminary Validation and Interim Methods



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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-560/5-82-006

2.

3. RECIPIENT'S ACCESSION NO.
PB83 127696

4. TITLE AND SUBTITLE
Analytical Methods for By-Product PCBs--Initial Validation and Interim Protocols

5. REPORT DATE
October 11, 1982

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) Mitchell D. Erickson, John S. Stanley, Gil Radolovich, Kay Turman, Karin Bauer, Jon Onstot, Donna Rose, and Margaret Wickham

8. PERFORMING ORGANIZATION REPORT NO.
MRI Project No. 4901-A51

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
EPA 68-01-5915, Task 51

12. SPONSORING AGENCY NAME AND ADDRESS
U.S. Environmental Protection Agency
Office of Toxic Substances, Field Studies Branch
TS-798
Washington, DC 20460

13. TYPE OF REPORT AND PERIOD COVERED
Interim 4, 4/24-8/31/82

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES
The task manager is David P. Redford; the project officer is Frederick W. Kutz.

16. ABSTRACT
This document presents proposed analytical methods for analysis of by-product PCBs in commercial products, product waste streams, wastewaters, and air. The analytical method for commercial products and product waste streams consist of a flexible approach for extraction and cleanup of particular matrices. The ^{13}C-labeled PCB surrogates are added as part of a strong quality assurance program to determine levels of recovery. The wastewater method is based on EPA Methods 608 and 625 with revisions to include use of the ^{13}C-labeled PCB surrogates. The air method is a revision of a proposed EPA method for the collection and analysis of PCBs in air and flue gas emissions. Capillary or packed column gas chromatography/electron impact ionization mass spectrometry is proposed as the primary instrumental method. Response factors and retention times of 77 PCB congeners relative to tetrachlorobiphenyl-d_6 are presented in addition to statistical analysis to project validity of the data and extrapolation of relative response factors to all 209 possible congeners. Preliminary studies using the ^{13}C-labeled surrogates to validate specific cleanup procedures and to analyze several commercial products and product wastes indicate that the proposed analytical methods are both feasible and practical.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Polychlorinated biphenyls	Commercial waste	streams	
PCBs	Capillary column	gas chromatography	
Incidentally generated	Electron impact	ionization mass spectrometry	
Analytical protocols	EIMS		
Air	Response factors	, relative response factors	
Wastewater	Relative retenti	on times	
Commercial products	Surrogates		

18. DISTRIBUTION STATEMENT
Unlimited

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
243

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

ANALYTICAL METHODS FOR BY-PRODUCTS PCBs--PRELIMINARY VALIDATION AND INTERIM METHODS

By

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TASK 51

INTERIM REPORT NO. 4

EPA Contract No. 68-01-5915
MRI Project No. 4901-A(51)

October 11, 1982

For

U.S. Environmental Protection Agency
Office of Toxic Substances
Field Studies Branch
TS-798
Washington, D.C. 20460

Attn: Dr. Frederick W. Kutz, Project Officer
Mr. David P. Redford, Task Manager

PREFACE

This report presents the results of a preliminary method validation accomplished on MRI Project No. 4901-A, Task 51, "PCB Analytical Methodology Task," for the Environmental Protection Agency (EPA Prime Contract No. 68-01-5915) during the period April 24 to August 31, 1982.

The document was prepared by Drs. Mitchell D. Erickson (Task Leader) and John S. Stanley and Ms. Kay Turman, with assistance from Kathy Funk, Cindy Melenson, and Gloria Sultanik. The laboratory work was conducted by Kay Turman, and Donna Rose, with assistance from Steven Turner. The gas chromatography/mass spectrometry analysis was performed by Gil Radolovich, Margaret Wickham, Jon Onstot, and Arbor Drinkwine. Statistical analysis of the data was provided by Karin Bauer. Editorial comments were provided by Rudena Mallory and Jeanne Robson.

The EPA Task Manager, David Redford, has been especially helpful and encouraging. The helpful comments of Ann Carey, Frederick W. Kutz, and John Smith, all of EPA, are also appreciated.

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SECTION 1

INTRODUCTION

The Environmental Protection Agency (EPA) is in the process of preparing rules for regulation of certain polychlorinated biphenyls (PCB) which are generated as by-products in the manufacture of commercial products (U.S. EPA, 1982). This regulation is under the Toxic Substances Control Act (PL 94-469), and EPA's Office of Toxic Substances has been assigned the task of preparing the rule.

As part of the rule, EPA is suggesting analytical methods for PCBs in air (stack gas and fugitive emissions), wastewater, product waste streams, and final products to assist organizations seeking an exclusion under this rule. To assist EPA in this mission, Midwest Research Institute (MRI) was asked to prepare appropriate analytical methodologies. A literature review and recommendation of general analytical approaches (Erickson and Stanley, 1982; Stanley and Erickson, 1982) constituted the first phase. The second phase, reported here, covers initial method validation and preparation of interim methods. As part of the method validation, four ^{13}C-PCB surrogates were synthesized and are reported separately (Roth et al., 1982). The third phase will involve interlaboratory validation and method refinement.

This report presents the initial results of method validation for analysis of by-product PCBs in product and product waste samples. Specifically, gas chromatography/electron impact mass spectrometry retention time and response factor data for 77 PCB congeners for two different gas chromatography/mass spectrometry systems, recoveries from several proposed cleanup steps, and recoveries from industrial samples using a variety of the method options are presented.

SECTION 2

SUMMARY

The objective of this study was to present EPA with appropriate methodologies for the analysis of by-product PCBs in commercial products, product waste streams, wastewaters, and air. In addition, EPA requested preliminary analytical studies to provide data in support of the proposed methods.

This document presents proposed analytical methods for the analysis of by-product polychlorinated biphenyls in commercial products and product waste streams (Appendix B), wastewater (Appendix C), and air (Appendix D). The proposed methods are based on determination of PCBs using gas chromatography/electron impact mass spectrometry (GC/EIMS). Capillary column gas chromatography (CGC) and packed column gas chromatography (PGC) are presented as alternate approaches. The ^{13}C-labeled PCB surrogates are added to samples prior to any sample preparation to allow method flexibility for a wide spectrum of matrices. Recovery of the surrogates will allow determination of the quality of analytical data. This method is valid only if the surrogates are thoroughly incorporated into the matrix.

The analytical method for commercial products and product waste streams relies heavily on a strong quality assurance program consisting of use of four ^{13}C-labeled surrogate PCBs, blanks, duplicates, spiked samples, and quality control samples. The analytical methods for water and wastewater are based on EPA Methods 608 and 625, revised to include the use of the ^{13}C-labeled surrogates. Likewise, the air method is a revision of a proposed method for PCBs in air and flue gas emissions.

This document presents relative response factors (RRF) of 77 PCB congeners which were used to determine the average RRF for PCBs by homolog. Statistical analysis of the data was performed to check the validity of the response factor data and to extrapolate RRFs for the unavailable congeners. Relative retention time (RRT) data for the 77 PCB congeners are also presented. The RRF and RRT data were determined on both magnetic sector and quadrupole mass spectrometer systems.

Preliminary studies were undertaken to check the validity of the proposed methods for the analysis of PCBs in commercial products and product waste streams. Data are presented for analysis of individual cleanup procedures as well as for analysis of product and product waste samples. The data indicate that the proposed method is applicable and useful for analysis of the matrices studied. However, these studies are preliminary and additional validation is necessary and ongoing.

SECTION 3

EXPERIMENTAL

The method validation was conducted in three stages: (a) determination of GC/EIMS parameters for 77 PCB congeners; (b) validation of individual method steps with clean matrices; and (c) validation of selected method options with real samples.

PREPARATION OF PCB STOCK SOLUTIONS AND WORKING STANDARDS

Source of Standards

Seventy-seven PCB congeners were acquired from Ultra Scientific, Inc., Hope, Rhode Island, and Analabs, North Haven, Connecticut. Quality control gas chromatography/flame ionization detection (GC/FID) data for the specific isomers were requested to verify the 99% purity assigned to these compounds. The GC/FID data supported the reported purity. In addition, all available nuclear magnetic resonance spectra used for specific isomer identification were requested but not supplied.

Weighing Procedures

Accurate mass measurement required calibration of a Cahn microbalance with National Bureau of Standards (NBS) certified masses of 5 and 10 mg. The balance was calibrated with the NBS standards followed by calibration of an in-house working standard mass. The calibration of the microbalance with the NBS certified masses was witnessed by a representative of the MRI quality assurance office. The mass of the working standard was measured between all measurements of individual PCB isomers to ensure that the balance was operating accurately. A record of the measured working standard mass was kept in a laboratory notebook. The mean value for the working standard was 10.037 ± 0.002 mg (0.02% relative standard deviation). When all measurements were completed, the mass of the NBS certified standards was determined as a final measure of the accuracy of the Cahn microbalance.

Preparation of Solutions

Preparation of PCB standard stocks began after accurate performance of the Cahn balance was demonstrated with the certified NBS and daily working standard. An aluminum weighing pan was preshaped such that complete transfer of the weighing pan plus sample could be made directly into the appropriate dilution vessel. The Cahn balance was tared to compensate for the weight of the aluminum boat, and the PCB standards were added via a micro spatula. The mass of the particular PCB was determined with the Cahn balance.

The aluminum pan containing the PCB standard was transferred to the dilution vessel using clean forceps, taking care not to spill any of the sample. The dilution vessel was capped tightly until solvent was added.

All PCB congeners were dissolved in toluene (Burdick and Jackson, distilled in glass). Masses of 0.1 to 5 mg were dissolved in a total of 1.0 ml toluene while masses of approximately 10 mg and greater were dissolved in 5.0 ml toluene. The solvent was delivered volumetrically by pipette. Room temperature and solvent temperature were recorded at the time of standard dissolution. Volumetric pipettes used for solvent delivery were calibrated so that the most accurate determination of analyte concentration could be calculated. Toluene was pipetted into a tared vessel, and the total mass was measured. Density of the solvent at the specific room temperature was used to calculate the actual volume dispensed. This calibration was performed for all pipettes used for volumetric delivery of solvent. The stock solutions were sonicated in an ultrasonic bath for at least 15 sec after the volumetric addition of toluene to ensure complete dissolution of the PCBs. The solution level was etched on the side of the dilution vessel as a means of detecting losses by evaporation.

The individual PCB congeners were referred to by the congener number indicated in Table 1. The stable labeled PCBs, 3,3',4,4'-tetrachlorobiphenyl-d_6, 4-chlorobiphenyl-$^{13}C_6$, 3,3',4,4'-tetrachlorobiphenyl-$^{13}C_{12}$, 2,2',3,3',5,5',6,6,'-octachlorobiphenyl-$^{13}C_{12}$, and decachlorobiphenyl-$^{13}C_{12}$ were assigned congener numbers of 210 to 214, respectively, for the purpose of this work. Sample labels were generated in duplicate to identify the specific PCB isomer stock solution and to document entries in the laboratory notebook. Table 2 presents the dilute working solutions that were prepared for determination of the response factors for the PCB congeners. The working solutions were prepared as 10 ml total volume. Table 3 presents the approximate concentration of each congener that was in the dilute working standard used for response factor determination. Tetrachlorobiphenyl-d_6 was added to 1.0 ml of each solution as the internal standard. All stocks were added to the working solutions in volumes of 20, 200, 250, 400, 500, or 1,000 μl. The syringes were calibrated at these volumes. Calibration of the 10-ml volumetric flasks used for working standards was accomplished by measuring the difference between the mass of the empty flask and the mass of the flask plus toluene added to the appropriate dilution mark. The density of toluene at the correct solvent temperature was used to calculate the final volume of each solution.

The dilute working solutions were divided into multiple aliquots. One hundred micrograms of tetrachlorobiphenyl-d_6 was added to each of the 1.0-ml aliquots of the solutions that were used to establish CGC/EIMS response factors The remaining dilute working solutions were stored in at least four crimp seal vials and refrigerated. The solvent meniscus was marked in permanent form to note losses of solvents from evaporation or spills. All solutions, stock standards and working solutions, were stored in a refrigerator. All vials removed from storage were first brought to room temperature and then sonicated for at least 15 to 30 sec before removing any of the solution.

TABLE 1. NUMBERING OF PCB CONGENERS[a]

No.	Structure
	Monochlorobiphenyls
1	2
2	3
3	4
	Dichlorobiphenyls
4	2,2'
5	2,3
6	2,3'
7	2,4
8	2,4'
9	2,5
10	2,6
11	3,3'
12	3,4
13	3,4'
14	3,5
15	4,4'
	Trichlorobiphenyls
16	2,2',3
17	2,2',4
18	2,2',5
19	2,2',6
20	2,3,3'
21	2,3,4
22	2,3,4'
23	2,3,5
24	2,3,6
25	2,3',4
26	2,3',5
27	2,3',6
28	2,4,4'
29	2,4,5
30	2,4,6
31	2,4',5
32	2,4',6
33	2',3,4
34	2',3,5
35	3,3',4
36	3,3',5
37	3,4,4'
38	3,4,5
39	3,4',5
	Tetrachlorobiphenyls
40	2,2',3,3'
41	2,2',3,4
42	2,2',3,4'
43	2,2',3,5
44	2,2',3,5'
45	2,2',3,6
46	2,2',3,6'
47	2,2',4,4'
48	2,2',4,5
49	2,2',4,5'
50	2,2',4,6
51	2,2',4,6'
	Tetrachlorobiphenyls
52	2,2',5,5'
53	2,2',5,6'
54	2,2',6,6'
55	2,3,3',4
56	2,3,3',4'
57	2,3,3',5
58	2,3,3',5'
59	2,3,3',6
60	2,3,4,4'
61	2,3,4,5
62	2,3,4,6
63	2,3,4',5
64	2,3,4',6
65	2,3,5,6
66	2,3',4,4'
67	2,3',4,5
68	2,3',4,5'
69	2,3',4,6
70	2,3',4',5
71	2,3',4',6
72	2,3',5,5'
73	2,3',5',6
74	2,4,4',5
75	2,4,4',6
76	2',3,4,5
77	3,3',4,4'
78	3,3',4,5
79	3,3',4,5'
80	3,3',5,5'
81	3,4,4',5
	Pentachlorobiphenyls
82	2,2',3,3',4
83	2,2',3,3',5
84	2,2',3,3',6
85	2,2',3,4,4'
86	2,2',3,4,5
87	2,2',3,4,5'
88	2,2',3,4,6
89	2,2',3,4,6'
90	2,2',3,4',5
91	2,2',3,4',6
92	2,2',3,5,5'
93	2,2',3,5,6
94	2,2',3,5,6'
95	2,2',3,5',6
96	2,2',3,6,6'
97	2,2',3',4,5
98	2,2',3',4,6
99	2,2',4,4',5
100	2,2',4,4',6
101	2,2',4,5,5'
102	2,2',4,5,6'
103	2,2',4,5',6
104	2,2',4,6,6'
	Pentachlorobiphenyls
105	2,3,3',4,4'
106	2,3,3',4,5
107	2,3,3',4',5
108	2,3,3',4,5'
109	2,3,3',4,6
110	2,3,3',4',6
111	2,3,3',5,5'
112	2,3,3',5,6
113	2,3,3',5',6
114	2,3,4,4',5
115	2,3,4,4',6
116	2,3,4,5,6
117	2,3,4',5,6
118	2,3',4,4',5
119	2,3',4,4',6
120	2,3',4,5,5'
121	2,3',4,5',6
122	2',3,3',4,5
123	2',3,4,4',5
124	2',3,4,5,5'
125	2',3,4,5,6'
126	3,3',4,4',5
127	3,3',4,5,5'
	Hexachlorobiphenyls
128	2,2',3,3',4,4'
129	2,2',3,3',4,5
130	2,2',3,3',4,5'
131	2,2',3,3',4,6
132	2,2',3,3',4,6'
133	2,2',3,3',5,5'
134	2,2',3,3',5,6
135	2,2',3,3',5,6'
136	2,2',3,3',6,6'
137	2,2',3,4,4',5
138	2,2',3,4,4',5'
139	2,2',3,4,4',6
140	2,2',3,4,4',6'
141	2,2',3,4,5,5'
142	2,2',3,4,5,6
143	2,2',3,4,5,6'
144	2,2',3,4,5',6
145	2,2',3,4,6,6'
146	2,2',3,4',5,5'
147	2,2',3,4',5,6
148	2,2',3,4',5,6'
149	2,2',3,4',5',6
150	2,2',3,4',6,6'
151	2,2',3,5,5',6
152	2,2',3,5,6,6'
153	2,2',4,4',5,5'
154	2,2',4,4',5,6'
155	2,2',4,4',6,6'
156	2,3,3',4,4',5
157	2,3,3',4,4',5'
158	2,3,3',4,4',6
159	2,3,3',4,5,5'
160	2,3,3',4,5,6
	Hexachlorobiphenyls
161	2,3,3',4,5',6
162	2,3,3',4',5,5'
163	2,3,3',4',5,6
164	2,3,3',4',5',6
165	2,3,3',5,5',6
166	2,3,4,4',5,6
167	2,3',4,4',5,5'
168	2,3',4,4',5',6
169	3,3',4,4',5,5'
	Heptachlorobiphenyls
170	2,2',3,3',4,4',5
171	2,2',3,3',4,4',6
172	2,2',3,3',4,5,5'
173	2,2',3,3',4,5,6
174	2,2',3,3',4,5,6'
175	2,2',3,3',4,5',6
176	2,2',3,3',4,6,6'
177	2,2',3,3',4',5,6
178	2,2',3,3',5,5',6
179	2,2',3,3',5,6,6'
180	2,2',3,4,4',5,5'
181	2,2',3,4,4',5,6
182	2,2',3,4,4',5,6'
183	2,2',3,4,4',5',6
184	2,2',3,4,4',6,6'
185	2,2',3,4,5,5',6
186	2,2',3,4,5,6,6'
187	2,2',3,4',5,5',6
188	2,2',3,4',5,6,6'
189	2,3,3',4,4',5,5'
190	2,3,3',4,4',5,6
191	2,3,3',4,4',5',6
192	2,3,3',4,5,5',6
193	2,3,3',4',5,5',6
	Octachlorobiphenyls
194	2,2',3,3',4,4',5,5'
195	2,2',3,3',4,4',5,6
196	2,2',3,3',4,4',5,6'
197	2,2',3,3',4,4',6,6'
198	2,2',3,3',4,5,5',6
199	2,2',3,3',4,5,6,6'
200	2,2',3,3',4,5',6,6'
201	2,2',3,3',4,5,5',6'
202	2,2',3,3',5,5',6,6'
203	2,2',3,4,4',5,5',6
204	2,2',3,4,4',5,6,6'
205	2,3,3',4,4',5,5',6
	Nonachlorobiphenyls
206	2,2',3,3',4,4',5,5',6
207	2,2',3,3',4,4',5,6,6'
208	2,2',3,3',4,5,5',6,6'
	Decachlorobiphenyl
209	2,2',3,3'4,4',5,5',6,6'

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[a] Adapted from Ballschmiter K, Zell M. 1980. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. Composition of technical Aroclor- and Clophen-PCB mixtures. Fresenius Z. Anal Chem 302:20-31.

TABLE 2. WORKING SOLUTIONS FOR PCB RESPONSE FACTORS

PCB homolog	PCB congener no.													
	Soln. no. 1	Soln. no. 2	Soln. no. 3	Soln. no. 4	Soln. no. 5	Soln. no. 6	Soln. no. 7	Soln. no. 8	Soln. no. 9	Soln. no. 10	Soln. no. 11	Soln. no. 12	Soln. no. 13	Soln. no. 14
Monochloro-	1	2	3											
Dichloro-	11	5	7	8	9	10	4	12	14	15				
Trichloro-	29	21	31	26	24	28	18	33	30					
Tetrachloro-	47	44	40	49	50	52	53	54	66	61	65	69	72	70,75,77
Pentachloro-	121	97	88	93	101	103	100	104	a	115	87	116	119	
Hexachloro-	136	129	128	137	138	141	143	151	139	153	154	155	156	
Heptachloro-	181	171	183	185										
Octachloro-	195	194	198	200	202	204								
Nonachloro-	207	208	206											
Decachloro-	209													
Total congeners	10	9	9	7	6	6	5	5	4	4	3	3	3	3

---

a Congener no. 112 was added to this solution but, on analysis, was determined to have a mass of 286 and appeared to be a diaminotrichlorobiphenyl. This congener was omitted from any further consideration.

TABLE 3. APPROXIMATE CONCENTRATION OF INDIVIDUAL PCB CONGENERS IN DILUTE WORKING STANDARDS[a]

PCB homolog	Concentration (μg/ml)
Monochlorobiphenyl	50
Dichlorobiphenyl	50
Trichlorobiphenyl	50
Tetrachlorobiphenyl	100
Pentachlorobiphenyl	100
Hexachlorobiphenyl	100
Heptachlorobiphenyl	100
Octachlorobiphenyl	200
Nonachlorobiphenyl	200
Decachlorobiphenyl	200

[a] Tetrachlorobiphenyl-d_6 was added to all solutions as an internal standard at ∿ 100 μg/ml.

Preparation of Calibration Standard and Spiking Mixtures

A mixture of 11 congeners was used for calibration. This solution was spiked into solvent for protocol step validation experiments and into product and product waste samples for standard addition experiments. These congeners were determined to be the best standards for quantitation calibration based on the average relative response factor for each PCB homolog, as will be discussed in Section 5.

Table 4 presents the composition of the 11-component solutions that are specified as the calibration standards, CSxxx, where the xxx is used to encode the nominal concentration in nanograms per milliliter. A more concentrated solution was diluted as necessary to prepare spiked samples and the appropriate standards for GC/EIMS analysis. The internal standard, tetrachlorobiphenyl-d_6, was added to all standards and final extracts before GC/EIMS analysis. The standards contained the four ^{13}C-labeled PCBs that were added from the spiking solution shown in Table 5.

GAS CHROMATOGRAPHY/ELECTRON IMPACT MASS SPECTROMETRY

The capillary gas chromatography parameters used are shown in Table 6. The quadrupole and magnetic sector mass spectrometer parameters used are shown in Tables 7 through 9. The characteristic ions for single ion monitoring and limited mass scanning are presented in Tables 10 through 12.

All data generated for relative response factors and concentration levels of PCBs in sample extracts were calculated based on the area of the primary quantitation ion specified in Table 10. The quantitation ions for the ^{13}C-labeled monochloro-, tetrachloro-, octachloro-, and decachlorobiphenyl were 194, 304, 442, and 510 Daltons, respectively. The pairings of analyte, calibration, and surrogate compounds are presented in Table 13.

DETERMINATION OF PCB RESPONSE FACTORS (GC/EIMS)

The response factors for 77 PCB isomers were determined by GC/EIMS using the working standards prepared as described in Tables 2 and 3. A high resolution capillary column (J&W Scientific Durabond DB-5, 15 m, 0.25 µm film thickness) was used for the separation of the PCB mixtures. Scanning mass spectrometry was used to calculate response factors for the PCB isomers present in each solution versus a known quantity of tetrachlorobiphenyl-d_6.

The quadrupole GC/EIMS system was tuned daily prior to any acquisition of data for PCB response factor calculations. The system was brought to operating temperature for at least 15 min. The fluorocarbon FC-43 was introduced to the ion source, and 176 and 502 Daltons were manually adjusted to a two-to-one ratio. This was accomplished by adjusting the multiplier voltage to 300 mV while monitoring 176 Daltons. A selected ion monitor acquisition was set up for 176 and 502 Daltons with a variance of 1 Dalton. The ratio of the two values was tuned to the two-to-one ratio as described above. The mass spectrometer was operated in the normal full scan acquisition mode after tuning with the FC-43. Approximately 100 ng of decafluorotriphenylphosphine was injected and the ratio of the values of 198/442 was monitored.

TABLE 4. CONCENTRATIONS OF CONGENERS IN PCB CALIBRATION STANDARDS (ng/ml)[a]

Homolog	Congener no.	CS1000	CS100	CS050	CS010
1	1	1,040	104	52	10
1	3	1,000	100	50	10
2	7	1,040	104	52	10
3	30	1,040	104	52	10
4	50	1,520	152	76	15
5	97	1,740	174	87	17
6	143	1,920	192	96	19
7	183	2,600	260	130	26
8	202	4,640	464	232	46
9	207	5,060	506	253	51
10	209	4,240	424	212	42
4	210 (IS)	255	255	255	255
1	211 (RS)	104	104	104	104
4	212 (RS)	257	257	257	257
8	213 (RS)	407	407	407	407
10	214 (RS)	502	502	502	502

---

[a] Concentrations given as examples only.

TABLE 5. COMPOSITION OF SURROGATE SPIKING SOLUTION (SS100) CONTAINING ^{13}C-LABELED PCBs[a]

Congener no.	Compound	Concentration (µg/ml)
211	(1',2',3',4',5',6'-$^{13}C_6$)4-chlorobiphenyl	104
212	($^{13}C_{12}$)3,3',4,4'-tetrachlorobiphenyl	257
213	($^{13}C_{12}$)2,2',3,3',5,5',6,6'-octachlorobiphenyl	395
214	($^{13}C_{12}$)decachlorobiphenyl	502

[a] Concentrations given as examples only.

TABLE 6. OPERATING PARAMETERS FOR CAPILLARY COLUMN GAS CHROMATOGRAPHIC SYSTEM

Parameter	Value
Gas chromatograph	Finnigan 9610
Column	15 m x 0.255 mm ID Fused silica
Liquid phase	DB-5 (J&W)
Liquid phase thickness	0.25 µm
Carrier gas	Helium
Carrier gas velocity	45 cm/sec[a]
Injector	On-column (J&W)
Injector temperature	Optimum performance[b]
Injection volume	1.0 µl[b]
Initial column temperature	110°C (2 min)[c]
Column temperature program	110° to 325°C at 10°C/min[d]
Separator	None[e]
Transfer line temperature	280°C

[a] Measured by injection of air or methane at 270°C oven temperature.

[b] For on-column injection, follow J&W instructions regarding injection technique.

[c] With on-column injection, the initial temperature equals the boiling point of the solvent; in this instance toluene.

[d] $C_{12}Cl_{10}$ elutes at 270°C. Programming above this temperature ensures a clean column and lower background on subsequent runs.

[e] Fused silica columns may be routed directly into the ion source to prevent separator discrimination and losses.

TABLE 7. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA FOR QUADRUPOLE CALIBRATION

Mass	Ion abundance criteria
197	Less than 1% of mass 198
198	100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

TABLE 8. OPERATING PARAMETERS FOR QUADRUPOLE MASS SPECTROMETER SYSTEM

Parameter	Value
Mass spectrometer	Finnigan 4023
Data system	Incos 2400
Scan range	95-550
Scan time	1 sec
Resolution	Unit
Ion source temperature	280°C
Electron energy[a]	70 eV
Trap current	0.2 mA
Multiplier voltage	-1,600 V
Preamplier sensitivity	10^{-6} A/V

[a] Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no separator is used.

TABLE 9. OPERATING PARAMETERS FOR MAGNETIC SECTOR MASS SPECTROMETER SYSTEM

Parameter	Value
Mass spectrometer	Finnigan MAT 311A
Data system	Incos 2400
Scan range	98-550
Scan mode	Exponential
Cycle time	1.2 sec
Resolution	1,000
Ion source temperature	280°C
Electron energy[a]	70 eV
Emission current	1-2 mA
Filament current	Optimum
Multiplier	-1,600 V

[a] Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no separator is used.

TABLE 10. CHARACTERISTIC SINGLE ION MONITORING (SIM) IONS FOR PCBs

Homolog	Ion (relative intensity)		
	Primary	Secondary	Tertiary
$C_{12}H_9Cl$	188 (100)	190 (33)	-[a]
$C_{12}H_8Cl_2$	222 (100)	224 (66)	226 (11)
$C_{12}H_7Cl_3$	256 (100)	258 (99)	260 (33)
$C_{12}H_6Cl_4$	292 (100)	290 (76)	294 (49)
$C_{12}H_5Cl_5$	326 (100)	328 (66)	324 (61)
$C_{12}H_4Cl_6$	360 (100)	362 (82)	364 (36)
$C_{12}H_3Cl_7$	394 (100)	396 (98)	398 (54)
$C_{12}H_2Cl_8$	430 (100)	432 (66)	428 (87)
$C_{12}HCl_9$	464 (100)	466 (76)	462 (76)
$C_{12}Cl_{10}$	498 (100)	500 (87)	496 (68)

Source: Rote JW, Morris WJ. 1973. Use of isotopic abundance ratios in identification of polychlorinated biphenyls by mass spectrometry. J Assoc Offic Anal Chem 56(1):188-199.

[a] None available.

TABLE 11. LIMITED MASS SCANNING (LMS) RANGES FOR PCBs

Compound	Mass range (Daltons)[a]
$C_{12}H_9Cl_1$	186-190
$C_{12}H_8Cl_2$	220-226
$C_{12}H_7Cl_3$	254-260
$C_{12}H_6Cl_4$	288-294
$C_{12}H_5Cl_5$	322-328
$C_{12}H_4Cl_6$	356-364
$C_{12}H_3Cl_7$	386-400
$C_{12}H_2Cl_8$	426-434
$C_{12}HCl_9$	460-468
$C_{12}Cl_{10}$	494-504
$C_{12}D_6Cl_4$	294-300
$^{13}C_6{}^{12}C_6H_9Cl$	192-196
$^{13}C_{12}H_6Cl_4$	300-306
$^{13}C_{12}H_2Cl_8$	438-446
$^{13}C_{12}Cl_{10}$	506-516

[a] Adapted from Tindall GW, Wininger PE. 1980. Gas chromatography-mass spectrometry method for identifying and determining polychlorinated biphenyls. J Chromatogr 196:109-119.

TABLE 12. CHARACTERISTIC IONS FOR ^{13}C-LABELED PCB SURROGATES

Compound	Ion (relative intensity)		
	Primary	Secondary	Tertiary
$^{13}C_6{}^{12}C_6H_9Cl$	194 (100)	196 (33)	-[a]
$^{13}C_{12}H_6Cl_4$	304 (100)	306 (49)	302 (78)
$^{13}C_{12}H_2Cl_8$	442 (100)	444 (65)	440 (89)
$^{13}C_{12}Cl_{10}$	510 (100)	512 (87)	514 (50)

[a] None available.

TABLE 13. PAIRINGS OF ANALYTE, CALIBRATION, AND SURROGATE COMPOUNDS

Analyte		Calibration standard		Surrogate	
Congener no.	Compound	Congener no.	Compound	Congener no.	Compound
1	2-$C_{12}H_9Cl$	1	2	211	$^{13}C_6$-4
2,3	3- and 4-$C_{12}H_9Cl$	3	4	211	$^{13}C_6$-4
4-15	$C_{12}H_8Cl_2$	7	2,4	211	$^{13}C_6$-4
16-39	$C_{12}H_7Cl_3$	30	2,4,6	212	$^{13}C_{12}$-3,3',4,4'
40-81	$C_{12}H_6Cl_4$	50	2,2',4,6	212	$^{13}C_{12}$-3,3',4,4'
82-127	$C_{12}H_5Cl_5$	97	2,2',3',4,5	212	$^{13}C_{12}$-3,3',4,4'
128-169	$C_{12}H_4Cl_6$	143	2,2',3,4,5,6'	212	$^{13}C_{12}$-3,3',4,4'
170-193	$C_{12}H_3Cl_7$	183	2,2',3',4,4',5',6	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
194-205	$C_{12}H_2Cl_8$	202	2,2',3,3',5,5',6,6'	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
206-208	$C_{12}HCl_9$	207	2,2',3,3',4,4',5,6,6'	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
209	$C_{12}Cl_{10}$	209	$C_{12}Cl_{10}$	214	$^{13}C_{12}Cl_{10}$

The response of 198 Daltons was 100% full scale and 442 Daltons was adjusted from 40 to 45% of the base peak. These criteria were met daily before data acquisition for response factor calculations was initiated.

All working standards were brought to room temperature and sonicated before injection into the GC/MS system. Solution No. 1 was analyzed daily as a means of normalizing response factors calculated from day to day. This allowed some compensation for differences in sensitivity due to subtle changes in the mass spectrometer operation from day to day. Also, a solution of tetrachlorobiphenyl-d_6 (internal standard) was analyzed separately. Four replicates of each working standard were analyzed to calculate variances of the response factors. The solutions were sonicated at least 15 sec prior to removal of sample for injection. The syringe and needle were rinsed with 200- to 300-µl of toluene between injections.

The gas chromatograph was operated at 110°C for 2 min, and programmed at 10°C/min to 325°C. One microliter injections were made with a J&W on-column injection system. Helium carrier flow was adjusted to 45 cm/sec.

The peak shape of the eluting PCBs was monitored. If excessive tailing was noted, the injection end of the fused silica capillary column was removed and shortened by at least 10 cm.

Tables 6, 7, and 8 present the instrument and operating parameters that were used to measure the response factors for the individual PCB isomers in the working solutions. Response factors (RF) were calculated using the area of the peaks for these ions according to the equation:

$$RF = \frac{A_{PCB}\ M_{IS}}{A_{IS}\ M_{PCB}}$$

where A_{PCB} = Area of the quantitation peak of the specific PCB,
M_{IS} = Mass (in nanograms) of the internal standard injected,
A_{IS} = Area of the quantitation peak of the internal standard, and
M_{PCB} = Mass (nanograms) of the specific PCB injected.

All relative response factor data were subjected to Student's t-test at the 95% confidence level to test for significant differences for day-to-day and solution-to-solution variances.

VALIDATION OF METHOD STEPS

A limited number of experiments were completed as preliminary validation steps for the proposed method presented in Appendices B through D. The experiment included evaluation of several of the cleanup procedures using solvent spiked with the ^{13}C-labeled surrogates and a mixture of PCB congeners representing each of the possible homologs. The laboratory cleanup procedures followed the protocol steps except where noted. One hexane solvent blank was analyzed by each procedure with the samples to monitor interferences and contamination.

All samples were analyzed by CGC/EIMS in the full scan mode using the Finnigan 4023 system. Tables 6, 7, and 8 present the instrumental parameters.

VALIDATION WITH PRODUCT AND PRODUCT WASTE SAMPLES

Sources of Samples

Product waste samples were received from Dow Chemical Company (Kent Hodges) and Vulcan Materials Company (Thomas Robinson) through the cooperation of the Chemical Manufacturers Association (Robert Fensterheim). These samples are aliquots of the materials used for the Chemical Manufacturers Association (CMA) round robin study (CMA, 1982). The CMA and associates supplied samples of chlorinated benzene waste streams, mixtures of chlorinated benzenes, composite waste streams from a chlorinated aliphatic process and a benzene column bottom sample. Table 14 presents an inventory of all the samples received.

Product samples were received from the Dry Color Manufacturers Association (J. Lawrence Robinson and Maria DaRoche). These samples included diarylide yellow, phthalocyanine green, and phthalocyanine blue pigments that were used in the Dry Color Manufacturers Association (DCMA) round robin study of an analytical method, reported by the DCMA (1981). These samples are also included in the inventory in Table 14.

The samples supplied by industry are examples of the samples which will be analyzed using the method in Appendix B. However, since no attempt was made to span the range of products and product wastes, the samples analyzed do not include all matrices which an analyst could encounter.

Experimental Design

Table 15 presents an overview of the preliminary method validation samples. The samples from Table 14 that were used for these studies included the chlorinated benzene waste stream, CMA-A; the benzene column bottom sample, CMA-E; and the yellow, blue, and green pigment samples, DCMA-1, DCMA-4, and DCMA-8, respectively. Blind quantitation standards and quality control samples were prepared by the MRI quality control staff either through spiked addition or by dilution of particular sample matrices. Other quality control procedures included the analysis of duplicate samples and blanks and the validation of cleanup steps. Two sets of samples were prepared and run at separate times. This first sample set us designated by numbers 10 through 110 and the second sample set is designated by numbers 2001 through 2210Q in Table 15.

The sample preparations ranged from addition of the ^{13}C-labeled surrogates followed by dilution and injection, to preparation of pigment samples via sulfuric acid dissolution and hexane extraction or methylene chloride extraction with Florisil cleanup.

TABLE 14. COMMERCIAL PRODUCT AND PRODUCT WASTE STREAM SAMPLES RECEIVED FOR PRELIMINARY METHOD VALIDATION STUDIES[a]

Sample no.	Quantity	Sample description	Sample source
CMA-A	100 ml	Chlorinated benzene waste stream	Dow Chemical Co.
CMA-B	100 ml	Mixture of chlorinated benzenes with Aroclor 1254 spike	Dow Chemical Co.
CMA-C	100 ml	Blind spike of CMA-B with the addition of 64 ppm of PCB isomers	Dow Chemical Co.
CMA-A	5 ml	Chlorinated benzene waste stream	Vulcan Materials Co.
CMA-B	5 ml	Mixture of chlorinated benzenes with Aroclor 1254 spike	Vulcan Materials Co.
CMA-C	5 ml	Blind spike of CMA-B with the addition of 64 ppm of PCB isomers	Vulcan Materials Co.
CMA-D	5 ml	Composite waste stream sample from a chlorinated aliphatic process	Vulcan Materials Co.
CMA-E	5 ml	Benzene column bottoms sample	Vulcan Materials Co.
DCMA-1	100 g	Diarylide yellow pigment	DCMA
DCMA-4	100 g	Phthalocyanine green pigment	DCMA
DCMA-6	100 g	Phthalocyanine blue pigment	DCMA
DCMA-8	100 g	Phthalocyanine blue pigment	DCMA
DCMA-9	100 g	Phthalocyanine green pigment	DCMA

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[a] Aliquots of CMA-A, CMA-B, and CMA-C were received from two sources, who indicated that they were identical. MRI has assumed that both aliquots are the same.

TABLE 15. PRELIMINARY METHOD VALIDATION SAMPLES

Sample no.	Description	Preparation	Dilution factor
10	CMA-A[a]	0.1 g/10 ml hexane	1/100
20A	CMA-A	0.1 g/10 ml hexane	1/100
20B	CMA-A	0.1 g/10 ml hexane	1/100
60	Hexane blank	None	None
110	CMA-E	None	None
2001	Hexane blank	None	None
2005	CMA-A[a]	0.1 g/1 ml hexane	1/10
2010	CMA-A	0.1 g/1 ml hexane	1/10
2020	CMA-A	0.1 g/1 ml hexane	1/10
2025Q	CMA-A	0.5-0.2 g/1 ml hexane	∼ 1/10
2030	CMA-A + CS002	0.1 g/1 ml hexane	1/10
2040	CMA-A + CS005	0.1 g/1 ml hexane	1/10
2050	CMA-A + CS010	0.1 g/1 ml hexane	1/10
2060Q	CMA-A + CSXXX[b]	0.1 g/1 ml hexane	1/10
2070Q	CSxxx	None	None
2080	Blank	DCMA-A	1/10
2090	CMA-A[b]	DCMA-A (0.1 g)	1/10
2100	Blank	DCMA-B	1/10
2110	CMA-A[b]	DCMA-B (0.1 g)	1/10
2120	Blank	Base	1/10
2130	CMA-A	Base (0.1 g)	1/10
2135	DCMA-1[a]	DCMA-B (1.0 g)	1/100
2140	DCMA-1	DCMA-B (1.0 g)	1/100
2150	DCMA-1	DCMA-B (1.0 g)	1/100
2160	DCMA-1 + no. 11 (50 ppm)	DCMA-B (1.0 g)	1/200
2170Q	DCMA-1 + no. 11 (20-80 ppm)	DCMA-B (1.0 g)	1/200
2175	DCMA-4	DCMA-B	1/100
2180	DCMA-4	DCMA-B	1/100
2185	DCMA-4[a]	DCMA-B	1/100
2190	DCMA-8	DCMA-A	1/50
2195	DCMA-8[a]	DCMA-A	1/50
2200Q	DCMA-8	DCMA-A	1/50
2210Q	CSxxx	None	None

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[a] No surrogates added to assess any background interferences for these compounds.

[b] Prepared from aliquot received from Dow Chemical Company; all other CMA-A samples prepared from aliquot received from Vulcan Materials Company.

The CMA-A and CMA-E samples were each analyzed after 1/10 or 1/100 dilution, depending on the operating sensitivity of the mass spectrometer. The CMA-A chlorinated benzene waste was the most extensively studied matrix of the available samples. Sample preparation included the simple dilution described above with and without the addition of the four surrogates. The samples prepared without surrogates allowed measurement of the background that might interfere with the four surrogate compounds. Duplicate samples of the CMA-A were analyzed at the same dilution in two separate experiments. The CMA-A matrix was also analyzed by standard addition methods with total spiked PCB levels of the 11-compound spiking solution (CS050) at approximately 70, 140, and 270 ng/sample. The CMA-A matrix was also prepared using the sulfuric acid and ethanolic KOH procedures discussed in Section 9.3.2 of Appendix D, Cleanup of the Analytical Method: The Analysis of By-Product Chlorinated Biphenyls in Commercial Product and Product Wastes (Appendix B). Variations of the analytical procedures used by the Dry Color Manufacturers Association (1981) for the analysis of PCBs in various pigments were also applied to the CMA-A matrix. The DCMA procedures included acid dissolution followed by hexane extraction from the acid (DCMA Preparation A) and Florisil treatment of the concentrated sample matrix (DCMA Preparation B). The homogenization and centrifugation steps required by the DCMA-B procedure were not included for the CMA-A matrix. All samples except those representing blanks were spiked with the surrogates at levels of 100 to 500 ng and were mixed thoroughly before beginning the sample preparation. The typical CMA-A sample size was 0.1 g.

The diarylide yellow (DCMA-1), phthalocyanine green (DCMA-4), and pthalocyanine blue (DCMA-8) pigments were also studied in these preliminary validations. The yellow pigment was prepared according to the recommended DCMA-B procedure, while the green and blue pigments were analyzed following the DCMA-A procedure. The preparation of the pigments followed the DCMA procedures except that the preparation was scaled to 1 g of the yellow pigment instead of the recommended 5 g. Blanks, duplicates, and spiked samples were also analyzed with the set of DCMA samples.

Sample Analysis

All extracts were analyzed by capillary column gas chromatography/electron impact mass spectrometry (CGC/EIMS). Limited mass scanning (LMS) or selected ion monitoring (SIM) mass spectrometry methods were used for extract analysis, depending on the level of PCBs in the sample extracts and the complexity of the matrix. The parameters for analysis via CGC/LMS and CGC/ MS-SIM are presented in Tables 6 through 13.

SECTION 4

METHOD VALIDATION

PREPARATION OF ANALYTICAL METHODS

Analytical methods were prepared for the analysis of by-product PCBs in:

- Commercial products and product wastes (Appendix B).
- Air (Appendix C).
- Industrial wastewater (Appendix D).

The analysis of commercial products and product wastes was covered in one method since the diversity of matrices in both categories dictates the same generalized approach. Air was defined to include stack gases, fugitive emissions, and static (room, other container, or outside) air.

Commercial Products and Product Wastes Method

The objective was to devise an analytical method suitable for enforcement of the regulation concerning by-product PCBs in commercial products and product wastes. A detailed rationale for selection of the techniques used in the method may be found in a separate report (Erickson and Stanley, 1982).

Sample Workup--

The general approach taken with sample preparation (collection, preservation, extraction, and cleanup) was to provide a framework within which any reasonable technique could be used. This is the only acceptable approach to a method designed to cover "any" matrix.

The use of ^{13}C-labeled recovery surrogates in conjunction with GC/EIMS was judged to be the most suitable approach (Erickson and Stanley, 1982; Stanley and Erickson, 1982; Roth et al., 1982). Using the recovery surrogates, any losses of PCBs would be detected and could be corrected for in the calculation of the PCB concentration.

When surrogates are not fully incorporated into the matrix, their recovery will not be representative of the analyte PCB recoveries and recovery assessment will not be possible. It is incumbent upon the analyst to recognize this problem and use good scientific judgment with samples that present a potential problem. Nonextractable solid polymers may be an example of a matrix presenting incorporation problems.

PCB Determination--

As discussed elsewhere (Erickson and Stanley, 1982; Stanley and Erickson, 1982), GC/EIMS appears to be the only acceptable general technique for determining PCBs in commercial products and product wastes. The use of either capillary or packed column GC is permitted. While strong arguments are presented for both techniques (Stanley and Erickson, 1982), the analytical results should be comparable for both techniques provided proper instrument calibration and operation, analytical, and quality control procedures are followed as described in the analytical methods.

Quantitation--

The analytical objective of these methods is to determine if the sample contains quantifiable PCBs and, if so, at what concentration. On the assumption that a general knowledge of the congener distribution is important, reporting of the concentration by homolog is proposed in the reporting form. Since a "total PCB" value is also important for summary and comparative purposes, space for this value is also provided on the reporting form. Other reporting formats, including "largest isomer or resolvable peak" or "all peaks greater than a regulatory value," may be easily accommodated using different tabulations and reporting procedures.

The PCB concentrations found may be lower than the actual value due to nonquantitative recovery during extraction or cleanup. The measured recoveries of the surrogates may be used to derive a corrected concentration. The analyst must take care that the surrogates are thoroughly incorporated into the matrix prior to extraction, as discussed above. The analyst must also guard against improper corrections because of errors in surrogate quantitation. These errors may arise from background interferences. A more thorough discussion of quantitation options is presented in a previous report (Erickson and Stanley, 1982).

Air Method

The sample collection, preservation, extraction, and cleanup aspects were taken from the work of Haile and Baladi (1977). The determination, using GC/EIMS, is identical to that in the commercial products and product wastes method except that recovery surrogates are not used.

Wastewater Method

The water method is a direct modification of the commercial products and product wastes method. As noted in this method, the cleanup and extraction procedures for EPA Methods 608 (U.S. EPA, 1979b) and 625 (U.S. EPA, 1979a) may be used. It is anticipated that, unless conditions dictate otherwise, most analysts will choose this option.

Quality Control

Each method includes a strong quality control (QC) section. Given the complexity of the matrices and complexity of the analyte (209 compounds), the need for QC is evident. The various aspects of the QC section were designed assuming a reasonably large (10 to 100) batch of samples. For small batches of samples, the percentage of effort spent on QC can become sizeable.

Alternate Methods

The methods presented here are intended to be primary methods capable of generating the best quality data technologically feasible. The development and acceptability of secondary (alternate, equivalent, or screening) methods is not addressed in this report.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY OF PCBs

Analysis for PCBs requires the use of selected representative standard compounds since all 209 congeners are not available. One of the major disadvantages of many instrumental methods for PCB analysis is the large variance of the instrumental response factors for PCB congeners, both within a homolog and between homologs. These large differences in response factors create problems in selecting representative compounds for quantitation purposes. The response factors of 77 of the possible 209 PCB congeners measured by GC/EIMS are presented in Tables 16 and 17. The data suggests that the EIMS response factor variance among PCB congeners is small relative to other detectors such as the electron capture detector or negative chemical ionization mass spectrometry.

Relative Response Factors

Quadrupole Mass Spectrometer--

The relative response factors (RRF) of the 77 PCB congeners were determined with the Finnigan 4023 quadrupole mass spectrometer as discussed in the experimental section. The RRFs were determined two ways to assess the effects of instrumental variability. The replicate RRF determinations are the average of four replicate analyses for each of the PCB congeners, all determined on a single day to assess the variability of the measurement. The single RRF determinations are single values from an experiment in which all 14 solutions containing all 77 congeners were run on one day to minimize instrumental variability with time. The data are presented in Appendix A. The RRFs vary from approximately 0.2 for decachlorobiphenyl to 4.1 for 2-chlorobiphenyl. Figures 1 and 2 present a visual comparison of average replicate and single RRFs of PCB congeners determined as replicate measurements and as single measurements.

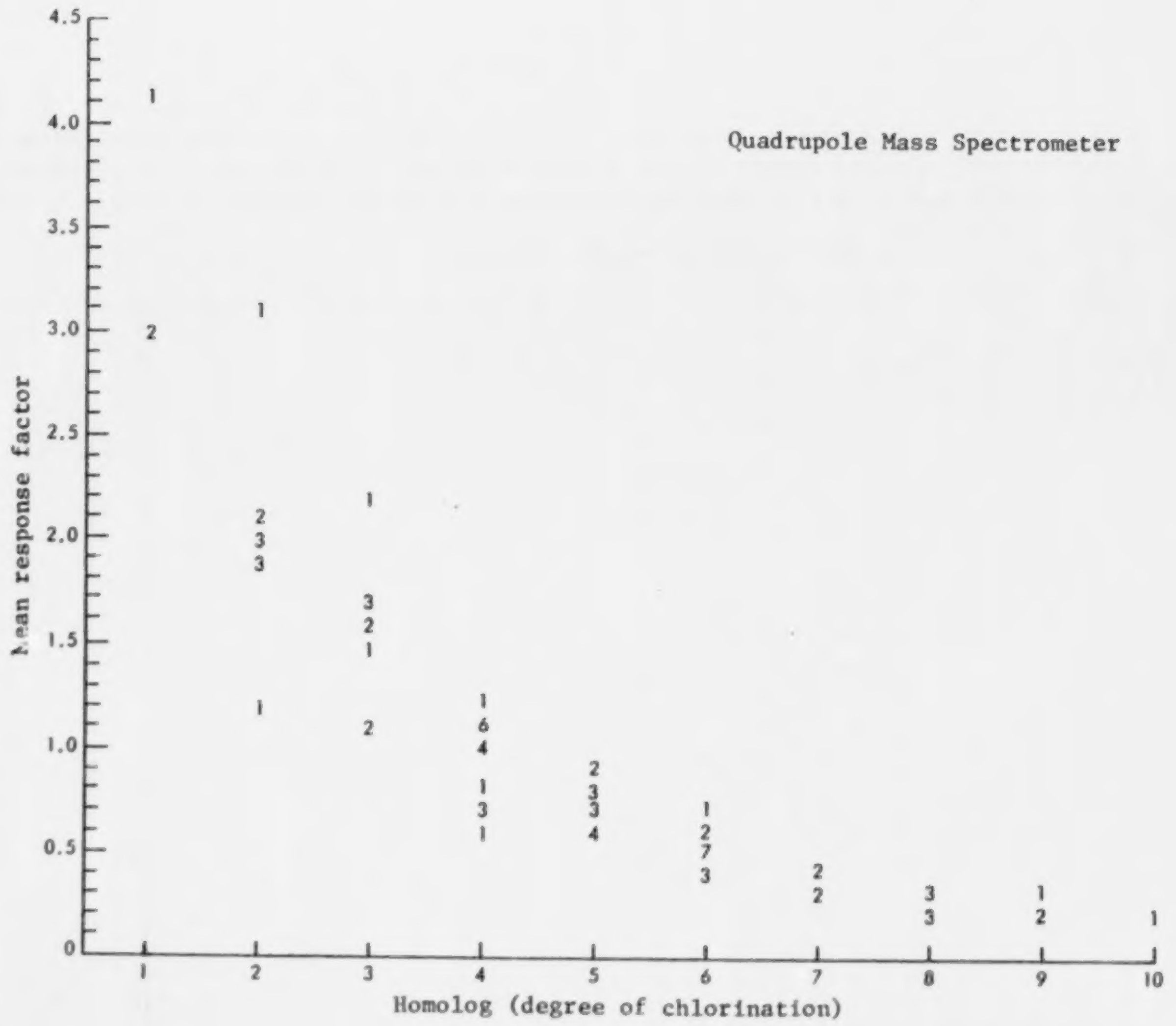

Figure 1. Plot of average response factor versus homolog for 77 PCB congeners. Each average is the mean response per congener, i.e., mean of four replicates with the Finnigan 4023 quadrupole mass spectrometer. This plot indicates the number of data points that overlap for specific isomers.

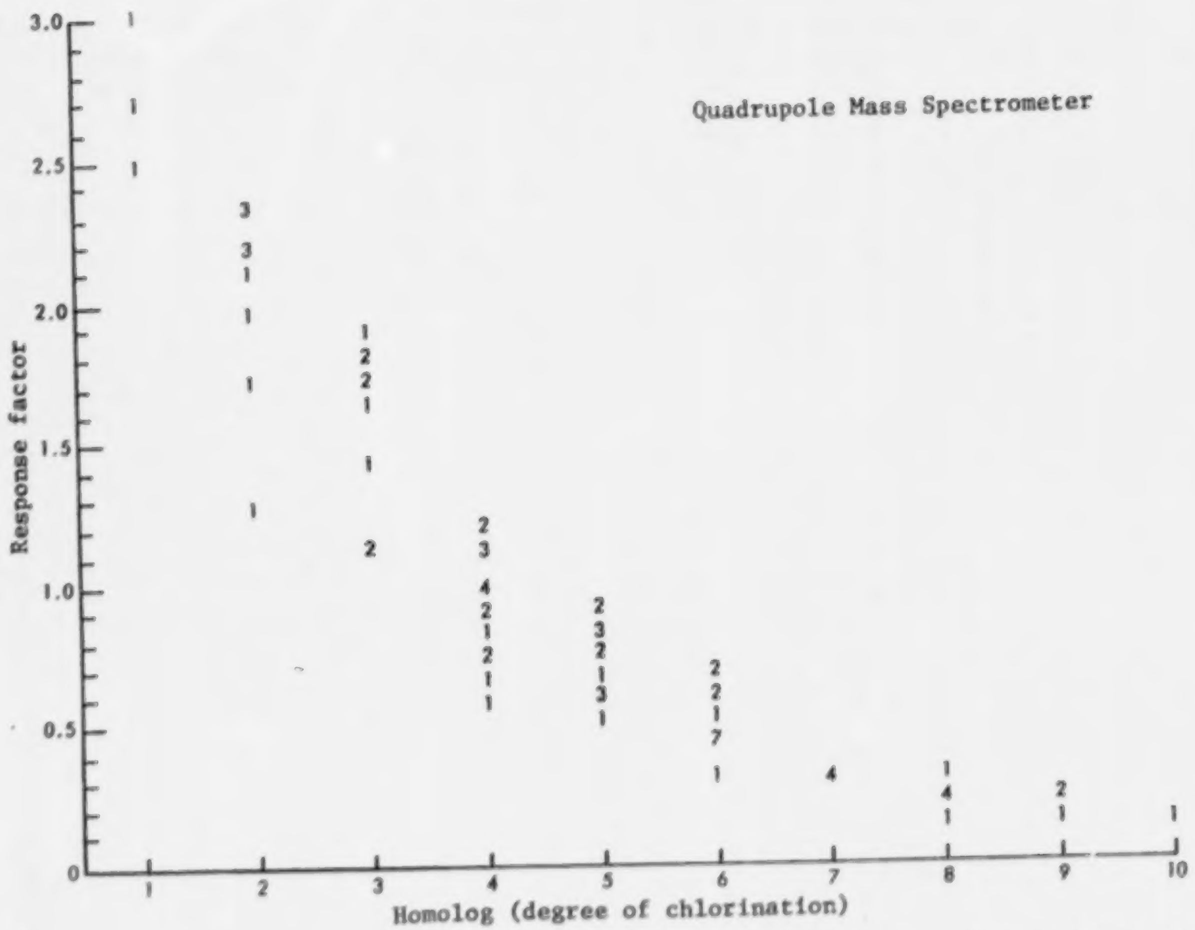

Figure 2. Plot of response factor per isomer versus homolog for 77 PCB congeners, determined on a single day. Each value is representative of single measurements of each congener with the Finnigan 4023 quadrupole mass spectrometer. This plot indicates the number of data points that overlap for specific isomers.

Table 16 is a summary of the RRF data, where the replicate and single measurements are averaged over all measured isomers for a homolog. The relative standard deviation (Table 16) for the replicate measurements reflects the variance of the average RRF for each isomer within a homolog. The absolute area of the internal standard, Congener No. 210, varied by only 4.4% for all solutions during the single day experiment, as compared to 9.9% for the 7 days required to complete the replicate analyses. The relative standard deviations based on the four replicate analyses for each of the PCB congeners, ranged from 0.4 to 9.1%, indicating the reproducibility of the injection for each solution.

The average response factors from replicate determinations and single measurements were subjected to a Student's t-test to determine if there were any significant differences in measured response factors. No significant difference was found for the average response factor values for any of the PCB homologs except the heptachlorobiphenyl isomers. A more detailed presentation of the Student's t-test for these values is presented in Table A-2 of Appendix A.

A solution of 3,3',4,4'-tetrachlorobiphenyl-d_6 (Congener No. 210) and Solution No. 1 (Table 2) were both analyzed daily. The solution of Isomer No. 210 was used to tune the quadrupole mass spectrometer to the desired working conditions. Solution No. 1 was used to determine fluctuations of response factors from day to day due to differences in instrumental operating parameters. Table 17 presents the data for single day replicate measurements and day-to-day determination of the response factors for the PCB congeners in Solution No. 1. The relative standard deviations calculated for the single day measurements are considerably lower than the relative standard deviations from day-to-day analyses. This is a reflection of the reproducibility on the part of the operator as well as of the stability of the quadrapole mass spectrometer system on a given day. The relative standard deviation calculated for day-to-day analyses is indicative of the variation that might be expected for routine analysis of PCBs.

A Student's t-test of the Solution No. 1 data (Table 17) indicated that there are significant differences in response factors from day to day compared to single day measurements for PCB Congener Nos. 1, 11, 29, and 207. A more detailed presentation of this t-test is presented in Table A-3 of Appendix A.

Magnetic Sector Mass Spectrometer--

The RRFs for the 77 PCB congeners were also determined with a Varian MAT 311A double focusing magnetic sector mass spectrometer. The RRF values were determined by single measurements of all congeners on a single day. The data are presented in Appendix A and summarized in Figure 3.

Extrapolation of Response Factor Data to All Congeners--

Since all 209 PCB congeners were not available for determination of RRFs, it was necessary to extrapolate the average RRF data to project the range of response factors that might be encountered. This extrapolation was based on the assumption that the number of measured isomers (n) are a representative sample of the entire set of the possible isomers (N). Thus it was assumed that the mean for the measured isomers (n) is an unbiased estimate of the mean for the possible isomers (N).

TABLE 16. AVERAGE RELATIVE RESPONSE FACTORS ($\overline{RRF}$) FOR 77 COMMERCIALLY AVAILABLE PCB CONGENERS MEASURED OVER SEVERAL DAYS AS FOUR REPLICATES EACH AND $\overline{RRF}$ FOR SINGLE MEASUREMENTS OF ALL CONGENERS IN A SINGLE DAY

PCB homolog	No. of isomers	$\overline{RRF}$ from replicate measurements[a]	Relative standard deviation (%)	$\overline{RRF}$ from single measurement[b]	Relative standard deviation (%)
Monochloro-	3	3.331	19.3	2.739	9.3
Dichloro-	10	2.027	22.0	2.048	15.7
Trichloro-	9	1.573	21.7	1.592	18.1
Tetrachloro-	16	0.950	18.4	0.946	20.0
Pentachloro-	12	0.720	16.7	0.725	17.6
Hexachloro-	13	0.513	15.1	0.500	19.1
Heptachloro-	4	0.361	6.6	0.308	8.0
Octachloro-	6	0.253	11.9	0.224	17.3
Nonachloro-	3	0.229	14.7	0.188	16.2
Decachloro-	1	0.213	2.8	0.179	-

[a] Four replicate measurements of the $\overline{RRF}$ were made for each isomer. For example, the three monochlorobiphenyl isomers were measured four times each. Hence, the $\overline{RRF}$ and relative standard deviation (%) were calculated from 12 distinct values.

[b] A single measurement for each of the 77 PCB congeners was completed in a single day. Hence, the $\overline{RRF}$ reported is the average of one measured RRF for each isomer within a homolog. For example, the $\overline{RRF}$ and relative standard deviation (%) reported for the monochlorobiphenyls were calculated from three distinct values.

TABLE 17. AVERAGE RELATIVE RESPONSE FACTORS ($\overline{RRF}$) FOR PCB CONGENERS IN SOLUTION 1 MEASURED AS REPLICATES ON A SINGLE DAY AND AS SINGLE MEASUREMENTS FOR DAY-TO-DAY BASIS[a]

Congener no.	Single day measurements[b]			Day-to-day measurements[c]		
	$\overline{RRF}$	Std. deviation	Relative std. deviation (%)	$\overline{RRF}$	Std. deviation	Relative std. deviation (%)
1	4.073	0.118	2.905	3.544	0.452	12.767
11	3.073	0.073	2.363	2.733	0.300	10.977
29	2.195	0.048	2.188	2.005	0.171	8.535
47	1.062	0.059	5.591	1.032	0.061	5.876
121	0.948	0.020	2.127	0.955	0.036	3.747
136	0.689	0.016	2.336	0.685	0.046	6.688
181	0.383	0.009	2.379	0.377	0.028	7.347
195	0.263	0.003	1.184	0.270	0.022	8.304
207	0.237	0.008	3.547	0.257	0.030	11.757
209	0.213	0.006	2.837	0.223	0.023	10.352

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[a] See Tables 6 and 8 for CGC/EIMS operating conditions.

[b] These values calculated from four replicates.

[c] These values calculated from 11 separate analyses.

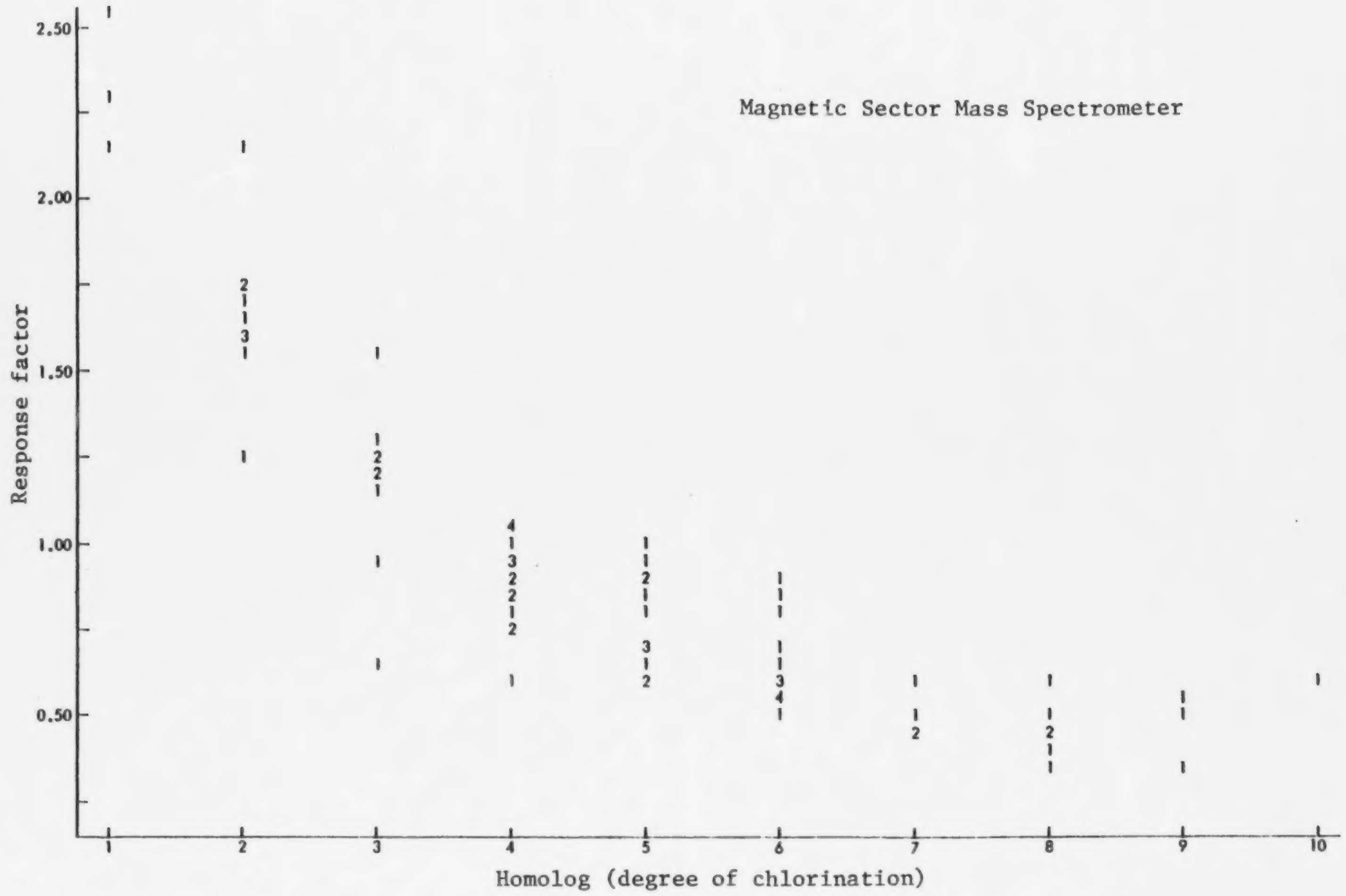

Figure 3. Plot of response factor per isomer versus homolog for 77 PCB congeners, determined on a single day. Each value is representative of single measurements of each congener with the Varian Mat 311A magnetic sector mass spectrometer. This plot indicates the number of data points that overlap for specific isomers.

Table 18 presents the upper and lower 95% confidence limits for the measured average RRFs. The extrapolation was necessary for the dichloro- through octachlorobiphenyl homologs. The projected upper and lower limits of the average RRF ranged from 13% for each PCB homolog for trichlorobiphenyls to approximately 6.5% for the dichlorobiphenyls. The projected ranges for the tetrachloro- to octachlorobiphenyls were between these values.

Comparison of Magnetic Sector and Quadrupole RRF Data--

The two instruments used operate on entirely different principles, so the results may represent the range of RRFs to be expected from these compounds on different instruments. Table 19 presents a summary of the data. As expected, the RRF trends are much different. Since quadrupole spectrometers discriminate at the high masses, the RRFs for high homologs (higer masses) are much lower than corresponding values for the magnetic detector spectrometer.

A statistical analysis of the data (Student's t-test presented in Table 4 of Appendix A) confirmed that the average RRFs are significantly different for many of the homologs. However, the relative standard deviations for the average RRF of each homolog are not significantly different. Thus, the extrapolation from a single calibration isomer to all isomers of a homolog should have similar precision for the two instrument types.

Relative Retention Times

Relative retention times (RRT) were also calculated from the data generated for relative response factor measurements with both the quadrupole and magnetic sector mass spectrometer instruments. All RRTs for each PCB congener were calculated versus 3,3',4,4'-tetrachlorobiphenyl-d_6. Figure 4 is a plot of the RRT data versus PCB homolog. All data points for the 77 PCB congeners measured with the quadrupole mass spectrometer are presented. This plot also indicates that the relative retention window for the dichloro- to octachlorobiphenyl homologs may be larger than that actually measured if more of the possible congeners were present.

Table 20 presents the observed range of RRTs for the 77 PCB congeners and additional congeners, identified only by homolog, in an Aroclor mixture (1016, 1254, 1260). These RRTs were established using a 15-m fused silica DB-5 capillary column. It must be recognized that the RRT windows on other columns may be substantially different. Table 20 also presents a projected RRT window for PCB anaysis. The overlap of the retention windows of each homolog must be considered in establishing an instrumental analysis approach to quantitation of the specific PCB homologs. This consideration has been accounted for in the GC/MS requirements for PCB analysis in Appendices B to D. The relative retention times of the 77 PCB congeners as determined with both the quadrupole and magnetic sector mass spectrometers are presented in tabular form in Appendix A.

TABLE 18. MEASURED AVERAGE RELATIVE RESPONSE FACTOR ($\overline{RRF}$) AND CORRESPONDING UPPER AND LOWER 95% CONFIDENCE LIMITS

PCB homolog	No. of possible isomers (N)	No. of available isomers (n)	Average measured response $\overline{RRF}$	Sample std. deviation (S)	Lower limit[a]	Upper limit[b]
Monochloro-	3	3	3.331	0.643	-	-
Dichloro-	12	10	2.027	0.447	1.896	2.158
Trichloro-	24	9	1.573	0.341	1.366	1.780
Tetrachloro-	42	16	0.950	0.175	0.877	1.023
Pentachloro-	46	12	0.720	0.120	0.654	0.786
Hexachloro-	42	13	0.513	0.078	0.474	0.552
Heptachloro-	24	4	0.361	0.024	0.326	0.396
Octachloro-	12	6	0.253	0.030	0.231	0.275
Nonachloro-	3	3	0.229	0.034	-	-
Decachloro-	1	1	0.213	-	-	-

[a] Lower 95% limit = $\overline{RRF} - \frac{ts}{\sqrt{n}}\left(1 - \frac{n}{N}\right)^{\frac{1}{2}}$

[b] Upper 95% limit = $\overline{RRF} + \frac{ts}{\sqrt{n}}\left(1 - \frac{n}{N}\right)^{\frac{1}{2}}$

TABLE 19. RELATIVE RESPONSE FACTORS MEASURED VERSUS 3,3',4,4'-TETRACHLOROBIPHENYL-d_6 BY ELECTRON IMPACT MASS SPECTROMETRY QUADRUPOLE (FINNIGAN 4023) AND MAGNETIC SECTOR (VARIAN MAT 311A) INSTRUMENTS

PCB homolog	No. of isomers measured	$\overline{RRF}$			
		Quadrupole		Magnetic sector	
		Mean	RSD[a] (%)	Mean	RSD[a] (%)
Monochloro-	3	2.739	9.3	2.329	8.5
Dichloro-	10	2.048	15.7	1.663	13.8
Trichloro-	9	1.592	18.1	1.167	21.3
Tetrachloro-	16	0.946	20.0	0.902	14.0
Pentachloro-	12	0.725	17.6	0.780	17.4
Hexachloro-	13	0.500	19.1	0.640	19.4
Heptachloro-	4	0.308	8.0	0.497	12.1
Octachloro-	6	0.224	17.3	0.463	15.3
Nonachloro-	3	0.188	16.2	0.467	22.5
Decachloro-	1	0.179	-	0.586	-

[a] Relative standard deviation.

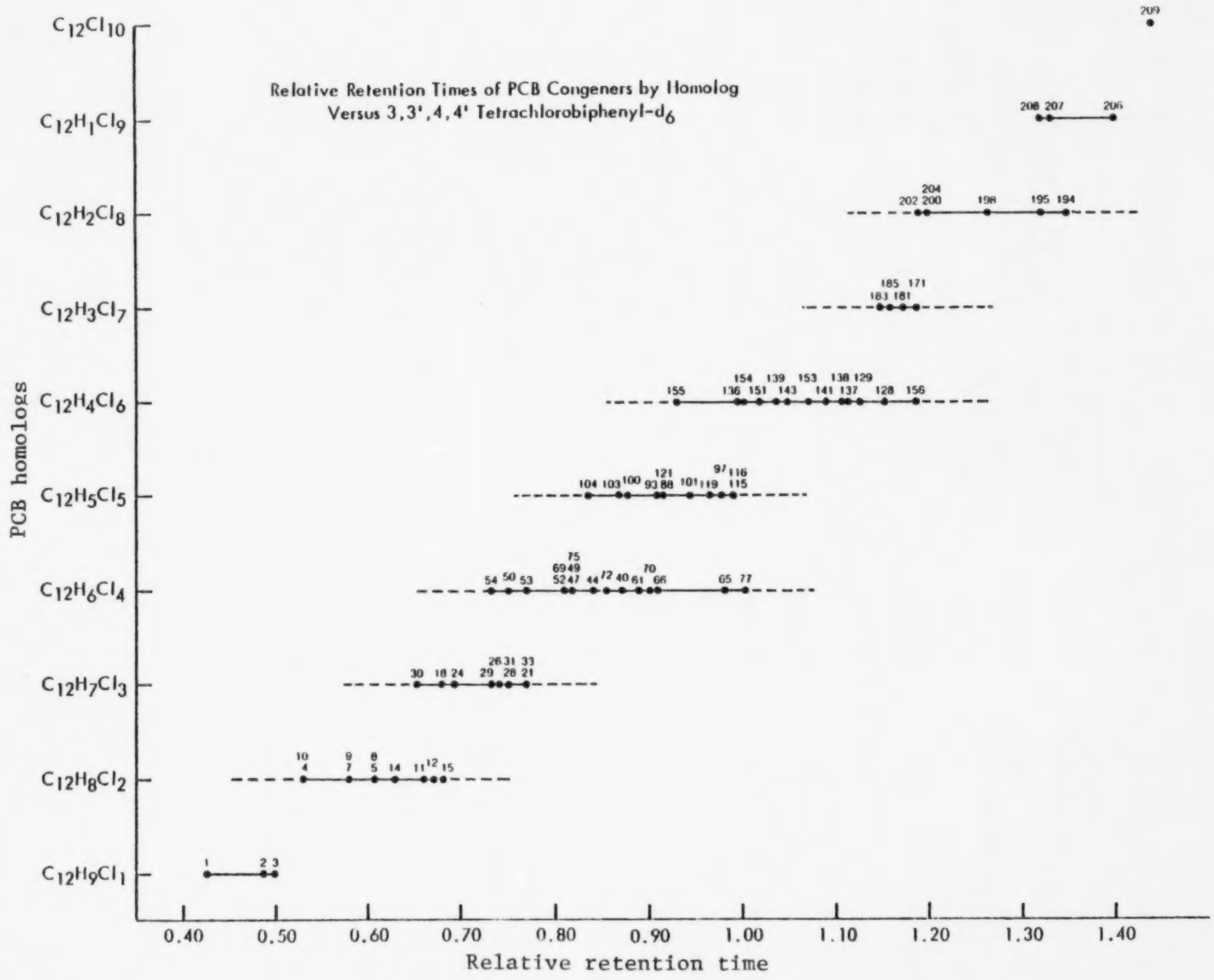

Figure 4. Retention times of 77 PCB congeners relative to 3,3',4,4'-tetrachlorobiphenyl-d_6 (RRT of 1.00). The dashed line indicates that not all of the possible isomers of a particular homolog were measured. Relative retention times were determined on a J&W DB-5, 15-m fused silica column in a Finnigan 4023 GC/EIMS system. Temperature program: 110°C for 2 min, then 10°C/min to 325°C.

TABLE 20. RELATIVE RETENTION TIME (RRT) RANGES OF PCB HOMOLOGS VERSUS d_6-3,3',4,4'-TETRACHLOROBIPHENYL

PCB homolog	No. of isomers measured	Observed range of RRTs[a]	Calibration solution Congener no.	Calibration solution Observed RRT[a]	Projected range of RRTs[b]
Monochlorobiphenyl	3	0.40-0.50	1 3	0.43 0.50	0.35-0.55
Dichlorobiphenyl	10	0.52-0.69	7	0.58	0.35-0.80
Trichlorobiphenyl	9	0.62-0.79	30	0.65	0.35-1.10
Tetrachlorobiphenyl	16	0.72-1.01	50	0.75	0.55-1.05
Pentachlorobiphenyl	12	0.82-1.08	97	0.98	0.80-1.10
Hexachlorobiphenyl	13	0.93-1.20	143	1.05	0.90-1.25
Heptachlorobiphenyl	4	1.09-1.31	183	1.15	1.05-1.35
Octachlorobiphenyl	6	1.19-1.36	202	1.19	1.10-1.50
Nonachlorobiphenyl	3	1.31-1.42	207	1.33	1.25-1.50
Decachlorobiphenyl	1	1.44-1.45	209	1.44	1.35-1.50

[a] The RRTs of the 77 congeners and a mixture of Aroclor 1016/1254/1260 were measured versus d_6-3,3',4,4'-tetrachlorobiphenyl (internal standard) using a 15-m J&W DB-5 fused silica column with a temperature program of 110°C for 2 min, then 10°C/min to 325°C, helium carrier at 45 cm/sec, and an on-column injector. A Finnigan 4023 Incos quadrupole mass spectrometer operating with a scan range of 95-550 Daltons was used to detect each PCB congener.

[b] The projected relative retention windows account for overlap of eluting homologs and take into consideration differences in operating systems and lack of all possible 209 PCB congeners.

Selection of Congeners for a Calibration Standard

The data generated from the RRF and RRT measurements were used to select the PCB congeners for an analytical quantitation/calibration standard for GC/EIMS analysis of PCBs. Selection of the standard compounds was based primarily on the ratio of the measured response factor to the average response factor for a particular homolog. The PCBs with RRFs closest to the average values were selected as standard compounds. In addition, the RRT was considered to assure that the selected PCB congeners did not coelute. Two monochlorobiphenyls were selected for the calibration standard because the average RRF and RRT did not clearly coincide with any of the three possible isomers. One isomer (2-chlorobiphenyl) had a substantially different RRF. This isomer was quantitated separately. 4-Chlorobiphenyl was selected as the calibration isomer for the two remaining isomers. Figure 5 is a CGC/EIMS chromatogram of the 11-component PCB calibration standard. The composition of this solution is identified in Tables 4 and 20 along with the observed RRT of each of the 11 congeners.

VALIDATION OF SELECTED CLEANUP STEPS

As part of the overall method validation, several of the cleanup techniques were validated. A mixture of the 11 calibration standard congeners and three recovery surrogates (the ^{13}C-octachlorobiphenyl was unavailable for these experiments) was diluted in an appropriate solvent and then subjected to the cleanup procedures as described in Appendix B. After the cleanup, the internal standard was added and the volume adjusted. The samples were analyzed by CGC/EIMS using a quadrupole spectrometer operated under the condition listed in Tables 6 through 8. Data were collected in the full scan mode and quantitated using the primary ions listed in Table 10 and the congener pairs listed in Table 13. A blank was run through the procedure alongside the recovery spikes. As expected, no PCBs except the internal standard were observed in the blanks.

The results for the 11 calibration congeners were calculated as percentage recovery. Tables 21 through 25 present the uncorrected recoveries, calculated using Equation 12-1 of Appendix B, using the internal standard (Congener No. 210); the actual percentage recoveries of the ^{13}C-labeled recovery surrogates, calculated using Equation 12-2 of Appendix B; and the corrected recoveries of the calibration congeners, calculated using Equation 12-3 of Appendix B.

Inspection of Tables 21 to 25 reveals that the accuracy of the corrected recoveries is higher than for the uncorrected recoveries (104% versus 77% average). On the other hand, the precision of the uncorrected recoveries is slightly higher than for the corrected recoveries (11% versus 9% relative standard deviation average). This is the expected trend since the uncorrected recovery relies on two GC/MS measurements (area of the PCB congener peak and area of the internal standard peak) and the corrected recovery relies on those two values and the area of the surrogate peak. Thus, these results indicate that accuracy is improved by recovery correction, at a sacrifice of precision.

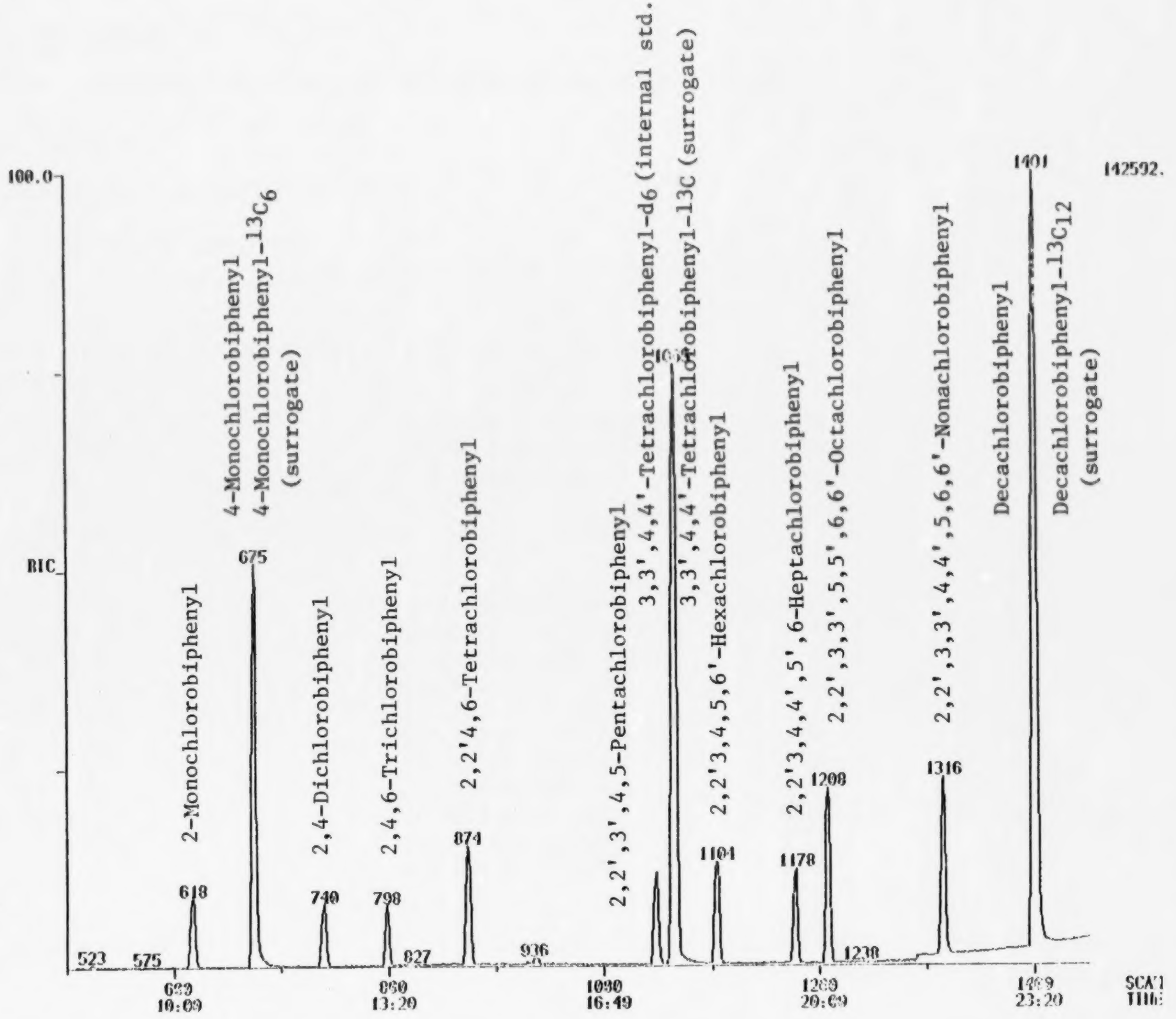

Figure 5. Capillary gas chromatography/electron impact ionization mass spectrometry (CGC/EIMS) chromatogram or the calibration standard solution required for quantitation of PCBs by homolog. This chromatogram includes PCBs representative of each homolog, three ^{13}C-labeled surrogates, and the deuterated internal standard. The concentration of all components and the CGC/EIMS parameters are presented in Tables 4, 5, 6 and 9.

TABLE 21. RECOVERY DATA FOR ACID CLEANUP[a]

Congener no.	PCB homolog	Total spike level (μg)	Spike 2 (% recovery) Uncorrected	Spike 2 (% recovery) Corrected[b]	Blank
1	Monochlorobiphenyl	0.52	100.0	142.4	ND[c]
3	Monochlorobiphenyl	0.50	83.4	118.8	ND
7	Dichlorobiphenyl	0.52	82.5	117.5	ND
30	Trichlorobiphenyl	0.52	NQ[d]	NQ	ND
50	Tetrachlorobiphenyl	0.76	78.0	89.6	ND
97	Pentachlorobiphenyl	0.87	99.5	114.2	ND
143	Hexachlorobiphenyl	0.96	81.2	93.2	ND
183	Heptachlorobiphenyl	1.30	85.9	98.5	ND
202	Octachlorobiphenyl	2.30	80.7	88.4	ND
207	Nonachlorobiphenyl	2.50	83.2	91.1	ND
209	Decachlorobiphenyl	2.10	87.3	95.7	ND
$\overline{X}$			86.2	104.9	-[e]
Standard deviation			7.5	17.7	-
Relative standard deviation (%)			9	17	-
211	$^{13}C_6$-monochlorobiphenyl	2.60	70.2	-	ND
212	$^{13}C_{12}$-tetrachlorobiphenyl	5.30	87.1	-	ND
214	$^{13}C_{12}$-decachlorobiphenyl	10.20	91.3	-	ND
$\overline{X}$			82.9	-	-
Standard deviation			11.2	-	-
Relative standard deviation (%)			13	-	-

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[a] Spike No. 1 not analyzed.

[b] Corrected via surrogate response.

[c] Not detected.

[d] Large background signal prevented quantitation of the compound.

[e] Not applicable.

TABLE 22. RECOVERY DATA FOR FLORISIL COLUMN CLEANUP

Congener no.	PCB homolog	Total spike level (μg)	Spike 1 (% recovery)		Spike 2 (% recovery)		Blank
			Uncorrected	Corrected[a]	Uncorrected	Corrected	
1	Monochlorobiphenyl	0.52	57.9	90.6	54.9	95.4	ND[b]
3	Monochlorobiphenyl	0.50	63.0	98.6	58.3	101.2	ND
7	Dichlorobiphenyl	0.52	66.0	103.2	60.0	104.4	ND
30	Trichlorobiphenyl	0.52	69.4	160.5	62.3	130.0	ND
50	Tetrachlorobiphenyl	0.76	70.7	163.6	62.4	130.3	ND
97	Pentachlorobiphenyl	0.87	73.4	169.7	66.1	138.1	ND
143	Hexachlorobiphenyl	0.96	72.6	168.1	67.0	140.1	ND
183	Heptachlorobiphenyl	1.30	76.6	177.2	72.3	151.0	ND
202	Octachlorobiphenyl	2.30	77.8	102.5	72.3	103.8	ND
207	Nonachlorobiphenyl	2.50	78.1	102.9	70.5	101.3	ND
209	Decachlorobiphenyl	2.10	77.7	102.4	72.8	104.5	ND
$\overline{X}$			71.2	130.9	65.4	118.2	-[c]
Standard deviation			6.7	35.8	6.2	19.8	-
Relative standard deviation (%)			9	27	10	17	-
211	$^{13}C_6$-monochlorobiphenyl	2.60	63.9	-	57.6	-	ND
212	$^{13}C_{12}$-tetrachlorobiphenyl	5.30	43.2	-	47.9	-	ND
214	$^{13}C_{12}$-decachlorobiphenyl	10.20	75.9	-	69.6	-	ND
$\overline{X}$			61.0	-	58.4	-	-
Standard deviation			16.5	-	10.9	-	-
Relative standard deviation (%)			27	-	19	-	-

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[a] Corrected via surrogate response.

[b] Not detected.

[c] Not applicable.

TABLE 23. RECOVERY DATA FOR FLORISIL SLURRY CLEANUP

Congener no.	PCB homolog	Total spike level (μg)	Spike 1 (% recovery)		Spike 2 (% recovery)		Blank
			Uncorrected	Corrected[a]	Uncorrected	Corrected	
1	Monochlorobiphenyl	0.52	80.5	96.0	71.1	92.9	ND[b]
3	Monochlorobiphenyl	0.50	81.2	96.8	72.7	94.8	ND
7	Dichlorobiphenyl	0.52	87.5	104.4	75.0	98.1	ND
30	Trichlorobiphenyl	0.52	NQ[c]	NQ	76.4	85.5	ND
50	Tetrachlorobiphenyl	0.76	90.0	91.6	80.1	89.6	ND
97	Pentachlorobiphenyl	0.87	96.0	97.6	83.5	93.5	ND
143	Hexachlorobiphenyl	0.96	95.5	97.2	82.0	91.6	ND
183	Heptachlorobiphenyl	1.30	95.1	96.8	79.8	89.3	ND
202	Octachlorobiphenyl	2.30	97.2	91.2	88.8	101.0	ND
207	Nonachlorobiphenyl	2.50	95.1	89.4	87.6	99.5	ND
209	Decachlorobiphenyl	2.10	96.2	90.4	83.7	95.2	ND
$\overline{X}$			91.4	95.1	80.1	93.7	-[d]
Standard deviation			6.3	4.5	5.8	4.7	-
Relative standard deviation (%)			7	5	7	5	-
211	$^{13}C_6$-monochlorobiphenyl	2.60	83.9	-	76.7	-	ND
212	$^{13}C_{12}$-tetrachlorobiphenyl	5.30	98.3	-	89.4	-	ND
214	$^{13}C_{12}$-decachlorobiphenyl	10.20	106.5	-	87.9	-	ND
$\overline{X}$			92.5	-	84.7	-	-
Standard deviation			7.5	-	6.9	-	-
Relative standard deviation (%)			8	-	8	-	-

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[a] Corrected via surrogate response.

[b] Not detected.

[c] Large background signal prevented quantitation of this compound.

[d] Not applicable.

TABLE 24. RECOVERY DATA FOR KOH CLEANUP

Congener no.	PCB homolog	Total spike level (μg)	Spike 1 (% recovery)		Spike 2 (% recovery)		Blank
			Uncorrected	Corrected[a]	Uncorrected	Corrected	
1	Monochlorobiphenyl	0.52	60.2	82.6	67.7	90.1	ND[b]
3	Monochlorobiphenyl	0.50	69.0	94.6	73.6	98.0	ND
7	Dichlorobiphenyl	0.52	73.5	100.8	77.5	103.3	ND
30	Trichlorobiphenyl	0.52	75.0	83.5	77.6	89.2	ND
50	Tetrachlorobiphenyl	0.76	79.7	88.7	80.7	92.9	ND
97	Pentachlorobiphenyl	0.87	85.8	95.4	85.0	97.7	ND
143	Hexachlorobiphenyl	0.96	84.0	93.4	85.0	97.7	ND
183	Heptachlorobiphenyl	1.30	81.2	90.3	81.3	93.5	ND
202	Octachlorobiphenyl	2.30	89.2	113.0	89.3	117.5	ND
207	Nonachlorobiphenyl	2.50	88.2	111.8	87.6	115.3	ND
209	Decachlorobiphenyl	2.10	69.9	88.6	71.9	94.6	ND
$\overline{X}$			77.8	94.8	79.7	99.1	-[c]
Standard deviation			9.1	10.2	6.8	9.5	-
Relative standard deviation (%)			12	11	9	10	-
211	$^{13}C_6$-monochlorobiphenyl	2.60	72.9	-	75.1	-	ND
212	$^{13}C_{12}$-tetrachlorobiphenyl	5.30	89.9	-	87.0	-	ND
214	$^{13}C_{12}$-decachlorobiphenyl	10.20	78.9	-	76.0	-	ND
$\overline{X}$			80.6	-	79.4	-	-
Standard deviation			8.6	-	6.6	-	-
Relative standard deviation (%)			11	-	8	-	-

---

[a] Corrected via surrogate response.

[b] Not detected.

[c] Not applicable.

TABLE 25. RECOVERY DATA FOR ALUMINA CLEANUP

Congener no.	PCB homolog	Total spike level (μg)	Spike 1 (% recovery)		Spike 2 (% recovery)		Blank
			Uncorrected	Corrected[a]	Uncorrected	Corrected	
1	Monochlorobiphenyl	0.52	63.1	97.1	61.1	101.0	ND[b]
3	Monochlorobiphenyl	0.50	60.0	92.2	58.4	96.2	ND
7	Dichlorobiphenyl	0.52	67.9	104.8	66.4	109.4	ND
30	Trichlorobiphenyl	0.52	NQ[c]	NQ	NQ	NQ	ND
50	Tetrachlorobiphenyl	0.76	67.2	97.2	66.3	102.2	ND
97	Pentachlorobiphenyl	0.87	70.4	101.9	68.3	105.4	ND
143	Hexachlorobiphenyl	0.96	69.4	100.4	67.5	104.2	ND
183	Heptachlorobiphenyl	1.30	75.8	109.7	75.1	115.8	ND
202	Octachlorobiphenyl	2.30	76.8	92.2	75.3	89.5	ND
207	Nonachlorobiphenyl	2.50	77.3	92.9	76.8	91.2	ND
209	Decachlorobiphenyl	2.10	74.0	88.9	78.3	93.0	ND
$\overline{X}$			70.2	97.8	70.1	100.8	-[d]
Standard deviation			5.9	6.5	6.9	8.4	-
Relative standard deviation (%)			8	7	10	8	-
211	$^{13}C_6$-monochlorobiphenyl	2.60	64.8	-	60.7	-	ND
212	$^{13}C_{12}$-tetrachlorobiphenyl	5.30	69.1	-	64.9	-	ND
214	$^{13}C_{12}$-decachlorobiphenyl	10.20	83.2	-	84.2	-	ND
$\overline{X}$			72.4	-	69.9	-	-
Standard deviation			9.6	-	12.5	-	-
Relative standard deviation (%)			13	-	18	-	-

---

[a] Corrected via surrogate response.

[b] Not detected.

[c] Large background signal prevented quantitation of this compound.

[d] Not applicable.

The preliminary data presented here contain an apparent anomaly: the low recovery of the ^{13}C-tetrachlorobiphenyl surrogate (Congener No. 212) from the Florisil column cleanup. These two data points contribute substantially to the imprecision of the surrogate recoveries and induce some very high (130 to 177%) corrected recoveries for the tri- through hepta- compounds. The experiment should be repeated.

VALIDATION OF THE PRODUCT AND PRODUCT WASTE METHOD WITH INDUSTRIAL SAMPLES

Strategy

Selected samples, obtained from industrial sources, were subjected to a variety of sample preparations as listed in Table 15 and then analyzed by CGC/EIMS. This section presents the results of this preliminary validation and, where possible, compares our values with those of previous analyses of the same sample. The results for quality control samples are also reported.

The most extensively studied matrix was the CMA-A chlorinated benzene waste stream sample. This particular sample was chosen because of the wide distribution of PCB homologs (mono- through decachlorobiphenyls). Sample preparation with this matrix included simple dilution, treatment with sulfuric acid, Florisil, and saponification with ethanolic potassium hydroxide. The CMA-A samples were analyzed in duplicate in two sets of experiments. The 11 PCB congeners used for calibration purposes were spiked into the CMA-A matrix for standard addition experiments. Blind spiked samples and quantitation standards, prepared by the MRI quality control personnel as analytical performance checks, were analyzed along with the other samples.

First Sample Set

Tables 26 and 27 present the uncorrected and corrected concentrations found for CMA-A samples in preliminary studies of the application of the proposed methods for commercial products and product wastes. Sample 10 was analyzed without surrogates to approximate the analytical procedure used by most other laboratories. As anticipated, the uncorrected values compare well with 20A and 20B, while the corrected values are slightly lower than the values for 10. Both corrected and uncorrected values for the duplicate samples 20A and 20B are in agreement. The values for samples 10, 20A, and 20B average about 400 µg/g. These values are higher than the mean of 280 µg/g reported in the CMA round robin but are in good agreement with the values (402 µg/g) reported by the sample supplier (Appendix E of Pittaway and Horner, 1982). The homolog distribution of our data agrees in general with the CMA data and the data that accompanied the samples.

Sample 110 (CMA-E) was determined to contain about 18 µg/g PCB (Table 28) mostly as the dichloro homolog. These results are slightly higher than the CMA round robin data, which had a mean reported value of 9 µg/g. The isomer distribution agrees with most of the CMA round robin data (Pittaway and Horner, 1982).

TABLE 26. UNCORRECTED PCB CONCENTRATIONS (μg/g) IN CMA-A SAMPLES

Congener no.	PCB homolog	10 Dilution, no surrog.	20A Dilution	20B Dilution
1	1	9	11	10
3	1	19	21	19
7	2	64	70	64
30	3	55	52	49
50	4	60	63	55
97	5	50	40	36
143	6	56	48	38
183	7	60	84	68
202	8	0	0	0
207	9	0.9	0	0
209	10	9.3	20	20
Total		414	408	358
211	1	NS[a]	96[b]	94
212	4	NS	108	97
214	10	NS	154	152

[a] No surrogates added.

[b] Surrogate recovery (percent).

TABLE 27. CORRECTED PCB CONCENTRATIONS (μg/g) IN CMA-A SAMPLES

Congener no.	PCB homolog	10 Dilution, no surrog.	20A Dilution	20B Dilution
1	1	NS[a]	11	11
3	1	NS	22	21
7	2	NS	73	68
30	3	NS	49	50
50	4	NS	58	57
97	5	NS	37	37
143	6	NS	44	39
183	7	NS	78	70
202	8	NS	0	0
207	9	NS	0	0
209	10	NS	13	13
Total			385	366

[a] No surrogates added.

Second Sample Set

CMA Product Waste Samples--

The corrected and uncorrected concentrations of the PCB homologs for duplicate CMA-A samples from a more extensive study are presented in Tables 29 and 30. Sample 2005 was spiked only with the internal standard so that any interferences corresponding to the ^{13}C-labeled PCBs could be measured. Samples 2010 and 2020 are duplicate samples of CMA-A. The four surrogate compounds were added to approximately 0.1 g of each sample. The mixture was diluted to 1.0 ml and the internal standard added. Sample 2025Q is a sample that was submitted for PCB analysis by the MRI quality control department. This sample was weighed by QC personnel and the final preparation completed as described for the previous samples. The MRI QC coordinator calculated the final concentration for 2025Q from the extract concentration of each PCB homolog and weight of the CMA-A sample recorded in the QC laboratory record book. The surrogate-corrected values reported for samples 2010 through 2025Q are in good agreement with the total PCB concentration and homolog distribution reported in the CMA round robin (Pittaway and Horner, 1982).

Tables 31 and 32 present the data from a standard addition experiment with the CMA-A sample matrix. The 11 PCB congener calibration standard was added to three separate aliquots of the CMA-A matrix to give spike levels ranging from approximately 20 to 100 µg of the monochlorobiphenyl and 50 to 200 µg of decachlorobiphenyl. Samples 2030, 2040, and 2050 were prepared in the analytical laboratory. Sample 2060Q was prepared as a blind spike of the CMA-A matrix by MRI quality control personnel. The uncorrected amount found did not increase linearly with the spike level. In fact, at the highest spike level (Sample 2050) the amounts found for each homolog were less than the spike. No explanation is immediately available for this data trend, although the low recoveries of the ^{13}C-octa- and tetrachlorobiphenyl surrogates indicated that the data are at best marginally valid.

Tables 33 and 34 present data for CMA-A samples that were subjected to three different cleanup methods (concentrated H_2SO_4, Florisil column chromatography, and saponification with alcoholic KOH). The data from the sulfuric acid cleanup was difficult to interpret because of interferences. As noted previously (Erickson and Stanley, 1982), the acid cleanup results in large losses of lower chlorinated PCB homologs. The poor recoveries of the surrogates shown in Table 33 are clearly outside of the QC criteria in Section 14.2.2 of Appendix B and indicate that the analyses are invalid. These results would not be reported as analyses for compliance with the proposed regulation.

All of the blank samples (2001, 1080, 2100, and 2120) were analyzed along with the sample discussed above and found to contain no detectable PCBs.

TABLE 28. UNCORRECTED AND CORRECTED PCB CONCENTRATIONS (μg/g) IN CMA-E SAMPLE (DILUTION PREPARATION)

Congener no.	PCB homolog	110 Uncorrected	110 Corrected
1	1	1.2	1.5
3	1	1.8	2.4
7	2	10.5	13.8
30	3	0	0
50	4	0	0
97	5	0	0
143	6	0.02	0.02
183	7	0	0
202	8	0.05	0.03
207	9	0	0
209	10	0.06	0.04
Total		13.4	17.7
211	1	76[a]	-[b]
212	4	103/91[c]	-
214	10	151	-

---

a Surrogate recovery (percent).

b Not applicable.

c Samples run twice on magnetic sector instrument for low and high masses. Congener no. 212 monitored in both runs.

TABLE 29. UNCORRECTED PCB CONCENTRATION (μg/g) IN THE CMA-A SAMPLE MATRIX (INTERNAL STANDARD CALCULATION)

PCB homolog CGC/EIMS analysis date	CMA-A 2005 8/4/82	CMA-A 2010 8/4/82	CMA-A 2020 8/5/82	CMA-A 2025[b] 8/5/82
Monochlorobiphenyl	26	23	37	40
Dichlorobiphenyl	35	28	41	48
Trichlorobiphenyl	17	14	46	50
Tetrachlorobiphenyl	20	31	33	36
Pentachlorobiphenyl	32	29	29	31
Hexachlorobiphenyl	29	23	21	22
Heptachlorobiphenyl	18	12	12	14
Octachlorobiphenyl	5.4	4.1	3.4	4.2
Nonachlorobiphenyl	2.6	2.2	2.0	3.5
Decachlorobiphenyl	12	10	9.7	11
Total PCB	197	176	234	260
Recovery (%) of Surrogate Compounds				
$^{13}C_6$-monochlorobiphenyl	NS[a]	64	84	89
$^{13}C_{12}$-tetrachlorobiphenyl[c]	NS	96	96	101
$^{13}C_{12}$-octachlorobiphenyl	NS	73	67	72
$^{13}C_{12}$-decachlorobiphenyl	NS	68	69	73

[a] NS = no surrogate added.

[b] Final concentration determined from sample weight recorded by QC coordinator.

[c] 302 Daltons used for quantitation.

TABLE 30. CORRECTED PCB CONCENTRATION (μg/g) IN THE CMA-A SAMPLE MATRIX

PCB homolog CGC/EIMS analysis date	CMA-A 2010 8/4/82	CMA-A 2020 8/5/82	CMA-A 2025Q[b] 8/5/82
Monochlorobiphenyl	37	44	44
Dichlorobiphenyl	44	48	53
Trichlorobiphenyl	15	47	49
Tetrachlorobiphenyl	33	34	34
Pentachlorobiphenyl	30	30	31
Hexachlorobiphenyl	24	21	22
Heptachlorobiphenyl	16	18	19
Octachlorobiphenyl	5.4	4.9	5.7
Nonachlorobiphenyl	3.1	3.0	4.8
Decachlorobiphenyl	15	14	16
Total PCB	223	264	280

a NS = no surrogates added.

b Final concentration determined from sample weight recorded by QC coordinator.

TABLE 31. UNCORRECTED PCB CONCENTRATION ($\mu g/g$) OF SPIKED CMA-A SAMPLES DETERMINED BY THE INTERNAL STANDARD QUANTITATION METHOD

PCB homolog	CMA-A 2030		CMA-A 2040		CMA-A 2050		CMA-A 2060Q		Blind quantitation standard[a]	
CGC/EIMS analysis date	Total sample concentration 8/5/82	Spike level	Total sample concentration 8/5/82	Spike level	Total sample concentration 8/6/82	Spike level	Total sample concentration 8/6/82	Spike level	Total sample concentration 8/6/82	Spike level
Monochlorobiphenyl	60	20	80	49	92	100	100	82	140	184
Dichlorobiphenyl	56	10	58	25	58	51	69	42	53	94
Trichlorobiphenyl	65	10	75	25	39	51	44	42	87	94
Tetrachlorobiphenyl	47	15	55	36	43	75	50	61	110	137
Pentachlorobiphenyl	48	17	58	42	64	86	73	70	140	157
Hexachlorobiphenyl	40	19	48	46	61	95	67	77	160	173
Heptachlorobiphenyl	40	25	58	62	87	130	87	100	340	234
Octachlorobiphenyl	46	45	82	110	100	230	110	180	560	414
Nonachlorobiphenyl	51	49	93	120	130	250	140	200	530	450
Decachlorobiphenyl	60	42	110	100	140	210	140	170	430	369
Total PCB	513	252	717	615	814	1,280	920	1,020	2,550	2,306
	Recovery (%) of surrogate compounds									
$^{13}C_6$-monochlorobiphenyl	89		79		76		93		88	
$^{13}C_{12}$-tetrachlorobiphenyl[b]	94		93		84		93		88	
$^{13}C_{12}$-octachlorobiphenyl	62		56		41		53		78	
$^{13}C_{12}$-decachlorobiphenyl	65		57		48		64		79	

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a Concentration in ng/ml rather than $\mu g/g$ since this sample was prepared by dilution of stock solutions of standards by QC personnel.

b 302 Daltons used for quantitation.

TABLE 32. CORRECTED PCB CONCENTRATION (μg/g) OF SPIKED CMA-A SAMPLES DETERMINED BY SURROGATE RECOVERY CORRECTION

PCB homolog	CMA-A 2030		CMA-A 2040		CMA-A 2050		CMA-A 2060		Blind quantitation standard 2070Q[a]	
	Total sample concentration	Spike conc.	Total sample concentration	Spike conc.	Total sample concentration	Spike conc.	Total sample concentration	Spike conc.	Total sample concentration	Spike conc.
CGC/EIMS analysis date	8/5/82		8/5/82		8/6/82		8/6/82		8/6/82	
Monochlorobiphenyl	67	20	100	49	120	100	110	82	160	184
Dichlorobiphenyl	63	10	74	25	76	51	74	42	60	94
Trichlorobiphenyl	70	10	80	25	46	51	47	42	99	94
Tetrachlorobiphenyl	50	15	58	36	52	75	53	61	130	137
Pentachlorobiphenyl	51	17	63	42	77	86	78	70	160	157
Hexachlorobiphenyl	43	19	52	46	72	95	72	77	190	173
Heptachlorobiphenyl	64	25	100	62	210	130	160	100	430	234
Octachlorobiphenyl	74	45	150	110	250	230	210	180	720	414
Nonachlorobiphenyl	81	49	170	120	330	250	270	200	680	450
Decachlorobiphenyl	91	42	180	100	280	210	220	170	540	369
Total PCB	650	250	1,030	620	1,510	1,280	1,290	1,020	3,190	2,310

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[a] Concentration in ng/ml rather than μg/g since this sample was a blind quantitation sample.

TABLE 33. PCB CONCENTRATION (μg/g) OF CMA-A SAMPLES TREATED WITH DIFFERENT CLEANUP PROCEDURES (INTERNAL STANDARD QUANTITATION)

PCB homolog	CMA-A 2090 acid cleanup	CMA-A 2110 Florisil cleanup	CMA-A 2130 alcoholic KOH cleanup
CGC/EIMS analysis date	8/9/82	8/9/82	8/9/82
Monochlorobiphenyl	ND[a]	4.4	31
Dichlorobiphenyl	4.4	14	44
Trichlorobiphenyl	0.4	31	44
Tetrachlorobiphenyl	25	18	25
Pentachlorobiphenyl	19	17	20
Hexachlorobiphenyl	7.9	5.6	6.3
Heptachlorobiphenyl	5.9	2.2	3.8
Octachlorobiphenyl	2.4	6.0	2.6
Nonachlorobiphenyl	38	2.4	2.6
Decachlorobiphenyl	16	9.5	6.4
Total PCB	119	110	186
Recovery (%) of surrogate compounds			
$^{13}C_6$-monochlorobiphenyl	74	8	145
$^{13}C_{12}$-tetrachlorobiphenyl[b]	0	0	367
$^{13}C_{12}$-octachlorobiphenyl	115	97	110
$^{13}C_{12}$-decachlorobiphenyl	173	129	64

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a ND = not detected.

b 302 Daltons used for quantitation.

TABLE 34. PCB CONCENTRATION (μg/g) OF CMA-A SAMPLES TREATED WITH VARIOUS CLEANUP PROCEDURES (SURROGATE COMPOUND CORRECTED)

PCB homolog CGC/EIMS analysis date	CMA-A 2090 acid cleanup 8/9/82	CMA-A 2110 Florisil cleanup 8/9/82	CMA-A 2130 alcoholic KOH cleanup 8/9/82
Monochlorobiphenyl	ND[a]	28	11
Dichlorobiphenyl	30	86	15
Trichlorobiphenyl	0.3 (0.2)[b]	200 (16)	15 (20)
Tetrachlorobiphenyl	17 (11)	110 (9.3)	8.4 (11)
Pentachlorobiphenyl	13 (8.3)	110 (8.9)	6.8 (9.0)
Hexachlorobiphenyl	5.3 (3.5)	3.5 (2.2)	2.9 (2.9)
Heptachlorobiphenyl	2.6	1.2	1.8
Octachlorobiphenyl	1.1	3.1	1.2
Nonachlorobiphenyl	17	1.2	1.2
Decachlorobiphenyl	3.9	3.1	4.2
Total PCB	90 (78)	546 (159)	68 (77)

[a] ND = not detected.

[b] $^{13}C_{12}$-tetrachlorobiphenyl was not quantifiable due to interferences. The values reported were calculated using $^{13}C_6$-monochlorobiphenyl. Values in parenthesis were calculated using $^{13}C_{12}$-octachlorobiphenyl.

DCMA Pigment Samples--

Eight DCMA pigment samples were analyzed following the preparation described in the experimental section (Table 15). The results are presented in Table 35. The diarylide yellow pigment (DCMA-1) was analyzed in duplicate and as a blind spike supplied by the MRI quality control department. This sample is reported to contain 3,3'-dichlorobiphenyl at levels of approximately 70 µg/g (Dry Colors Manufacturing Association, 1981). No analyte or surrogate PCBs were detected in the duplicate 1-g samples of the pigment and a known spike of the sample. The lack of detected PCBs indicates a loss of analytes in the sample preparation. The CGC/EIMS analysis of a sample of the yellow pigment spiked by MRI quality control personnel yielded an uncorrected concentration of 76 µg/g of 3,3'-dichlorobiphenyl based on the internal standard quantitation and a corrected concentration of 63 µg/g, based on 120% recovery of the $^{13}C_6$-4-monochlorobiphenyl surrogate. The level of the 3,3'-dichlorobiphenyl added by the QC personnel was reported to be 60 µg/g. Hence, the total dichlorobiphenyl concentration should have been approximatey 130 µg/g (70 µg/g endogenous plus 60 µg/g added).

The phthalocyanine green pigment (DCMA-4) was also analyzed in duplicate following dissolution and fractionation with a Florisil column. This pigment reportedly contains only decachlorobiphenyl at approximately 40 µg/g based on the results of the DCMA round robin study (Dry Color Manufacturing Association, 1981). Our analysis of duplicate samples yielded uncorrected concentration levels of 24 and 27 µg/g of decachlorobiphenyl by the internal quantitation method. The corrected concentration for both samples was 13 µg/g with recovery of the $^{13}C_6$-decachlorobiphenyl surrogate at 190 and 210%.

Phthalocyanine blue (DCMA-8) was also analyzed as a single sample. Pentachloro- and hexachlorobiphenyls were detected but the concentrations were below the quantitation limits for that particular day. The total PCB concentration of this pigment, as discussed in the results of the DCMA round robin (1981), is reported to be 90 µg/g.

The DCMA pigment sample analyses did not produce valid results. These data suggest that further development or validation of extraction/cleanup procedure would be necessary to provide acceptable PCB analyses of these samples. All of the blank samples (2001, 2080, and 2100) analyzed along with the DCMA samples were found to contain no detectable PCBs.

DISCUSSION

The determination of PCBs is a complex problem. The inaccessability of standards for all 209 congeners has traditionally been circumvented by the use of commercial mixtures (e.g., Aroclors) as standards. Quantitation has often been addressed in terms of relating the analyte to an Aroclor standard to give a "total PCB" concentration. Determination of PCBs synthesized as by-products in commercial products or product waste presents three special problems: (a) the analyte does not generally resemble a commercial PCB mixture, so quantitation against Aroclor standards would be incorrect; (b) the matrix often contains high concentrations of other chlorinated organics which are not easily separated during a cleanup procedure and which interfere with the qualitative and quantitative analysis; and (c) the matrix is undefined and can include gases, liquids, or solids of any purity and complexity.

TABLE 35. RECOVERY (%) OF CARBON-13 LABELED SURROGATE COMPOUNDS FROM DIARYLIDE YELLOW AND PHTHALOCYANINE BLUE AND GREEN PIGMENTS

PCB surrogate	DCMA-1 2140[a]	DCMA-1 2150[a]	DCMA-1 2160[b]	DCMA-1 2170Q[c]	DCMA-4 2175[d]	DCMA-4 2180[d]	DCMA-8 2190[e]	DCMA-8 2200Q[f]
$^{13}C_6$-Monochlorobiphenyl	ND[g]	ND	ND	120	ND	ND	ND	12
$^{13}C_{12}$-Tetrachlorobiphenyl	ND	ND	ND	ND	ND	ND	94	52
$^{13}C_{12}$-Octachlorobiphenyl	ND	ND	ND	200	120	107	92	71
$^{13}C_{12}$-Decachlorobiphenyl	ND	ND	ND	250	190	210	150	77

[a] Samples 2140 and 2150 are duplicates prepared by the DCMA-B method.

[b] Sample 2160 was spiked with 50 μg/g of 3,3'-dichlorobiphenyl and prepared by the DCMA-B method.

[c] Sample 2170Q was spiked by MRI quality control personnel with 3,3'-dichlorobiphenyl and was prepared by the DCMA-B method.

[d] Samples 2175 and 2180 are duplicates prepared by the DCMA-B method.

[e] Sample 2180 was prepared by the DCMA-A method.

[f] Sample 2200Q was weighed by MRI quality control personnel. An unknown mass of sample was supplied for preparation by the DCMA-A method.

[g] The four surrogate compounds were added but not detected.

In this situation, analytical methods require a different philosophy than the classic approach for a single analyte in a defined matrix where all steps, reagents, and apparatus are specified. The method proposed here leaves many of the analytical steps to the discretion of the analyst while ensuring the reliability of the results with a strong quality control program. Thus, an analyst familiar with general analytical techniques for a product, may readily adapt in-house extraction/cleanup procedures to incidental PCB analysis. Even when the recoveries are not optimized, the ^{13}C-labeled surrogate recoveries will mimic those of the analyte PCBs. As long as the ^{13}C recovery surrogates are thoroughly incorporated, their recoveries can be used to derive corrected analyte PCB concentrations.

Several of the method validation analyses presented above, especially Tables 33 and 35, illustrate the importance of the recovery surrogates in QC. The techniques employed are common methods validated for PCB analysis by other laboratories without the ^{13}C-surrogate data. Analyses of this type may have been used by a testing laboratory and erroneous results reported.

The complexity of the matrix and the high probability of chlorinated organic interferents precluded the use of GC/ECD. The best available technique is GC/EIMS. During the validation work presented above, the anticipated difficulty of qualitatitve and quantitative data interpretation was confirmed. In addition to the inherent problems resulting from extrapolation from a standard to several analytes, interpretation of the complex peak clusters is a tedious, subjective, and error-prone process. The volume of data for one sample is staggering; for sample 2110, 286 peaks were identified and integrated in the PCB mass chromatograms as shown in Figures 6 through 16. Of these, 58 peaks met the qualitative criteria and were identified as PCBs. Clearly different analysts will obtain different results for those peaks which marginally fit the qualitative criteria. This very high data density relative to other common GC/MS analyses has a much higher potential for error and mistakes. In addition it should be noted that, for many of the samples analyzed in this study, the data interpretation is more time-consuming than the rest of the analytical process.

The integration methods are also prone to error. Integration is always conducted interactively with the mass spectrometric data system, either manually or automatically. The selection of baseline criteria, background sensitivity, integration method (valley-to-valley, baseline-to-baseline, etc.), and retention window all affect automatic quantitation. The position of the cursor and integration method affect the manual quantitation results.

The day-to-day instrumental variability with quadrupole systems also appears to adversely affect data quality, despite tight calibration specifications. The magnitude of this error soruce should be further documented.

The above discussion presents some of our understanding of some of the major problems with analysis for by-product PCBs. Further work will be devoted to characterizing and reducing these problem areas. Even with forseeable improvements in the method, the data for by-product PCBs in many commercial product and product waste samples will exhibit low precision and accuracy.

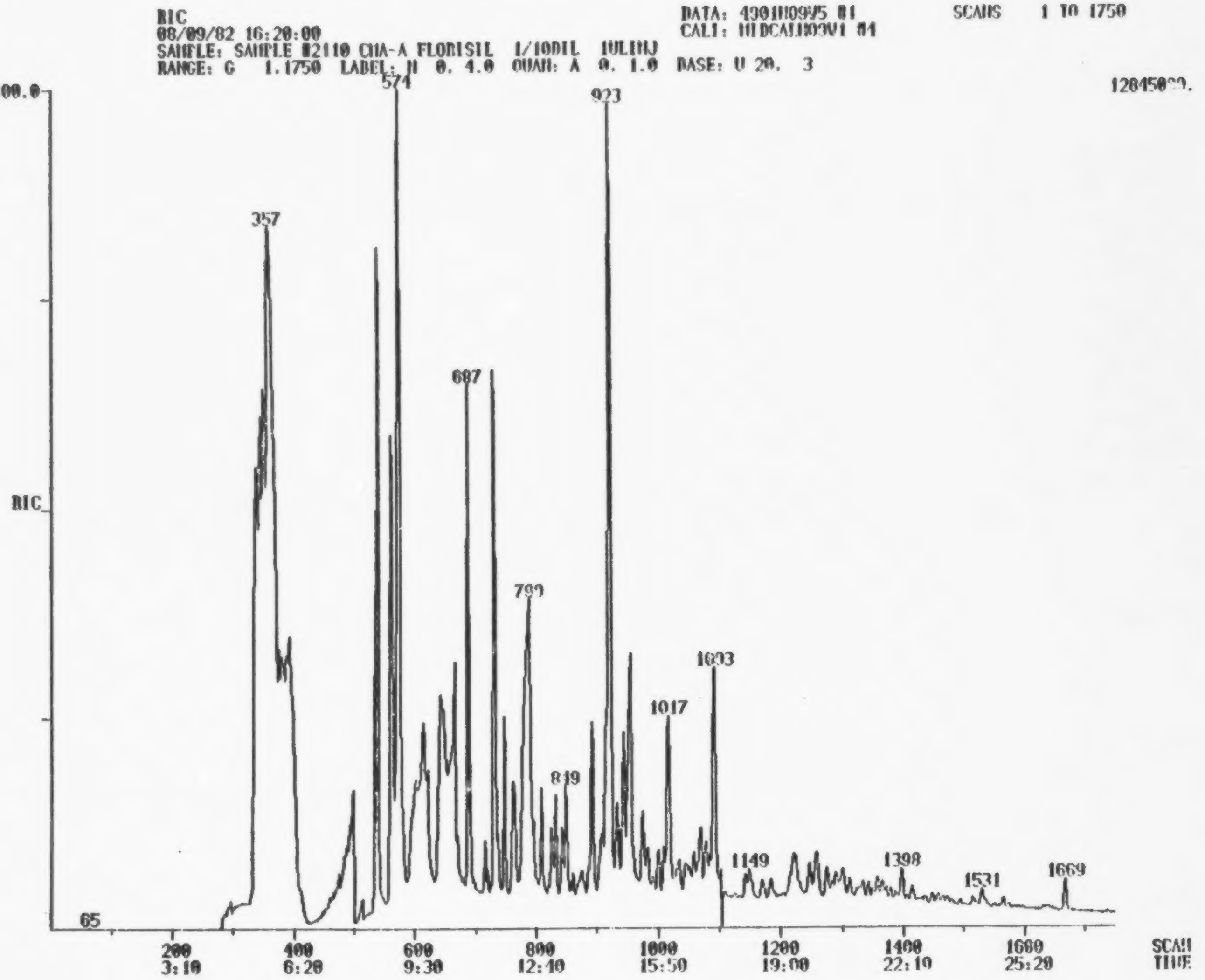


Figure 6. Reconstructed ion chromatogram for SIM analysis of the CMA-A sample No. 2110.

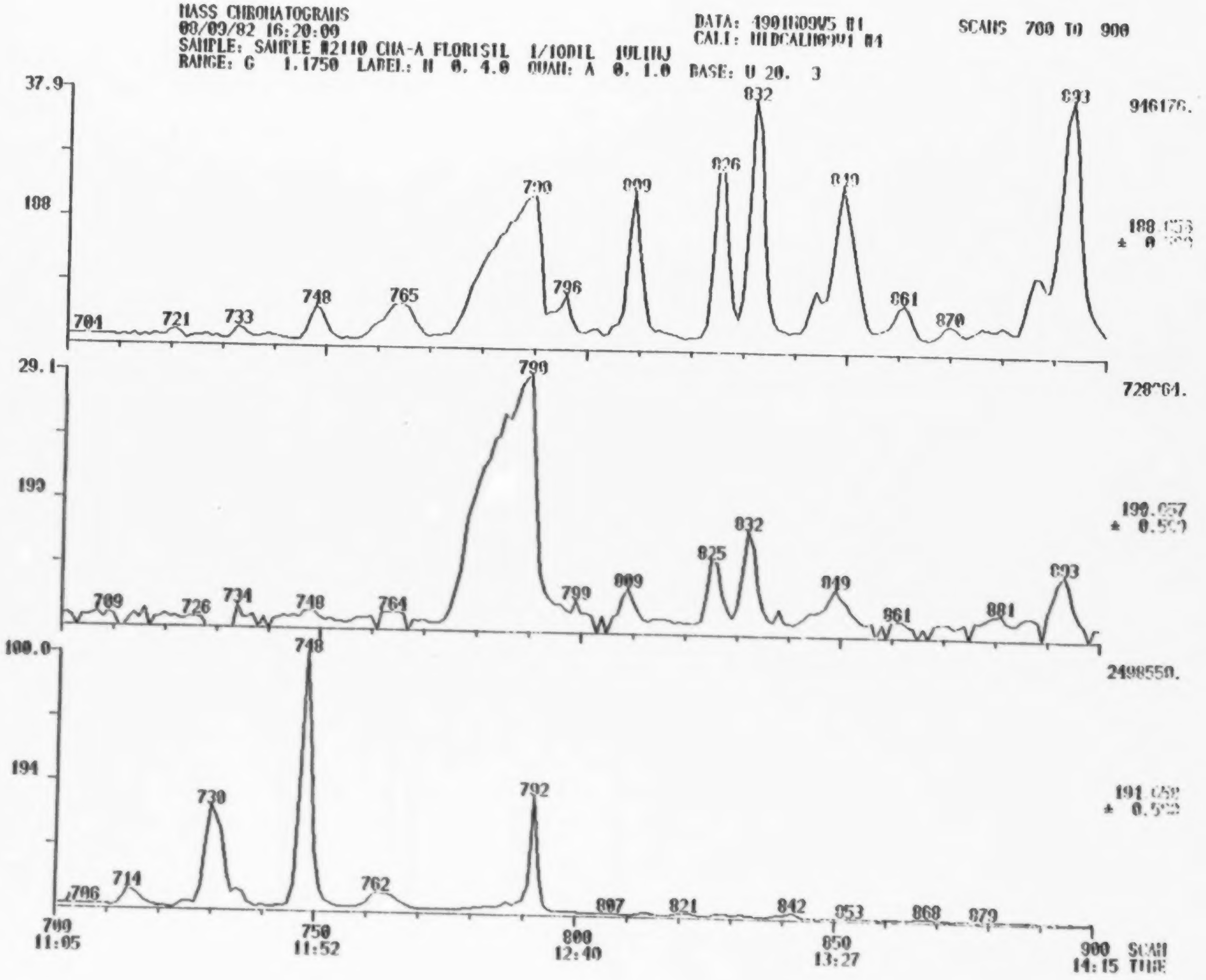


Figure 7. SIM ion plots for monochlorobiphenyls (188 and 190 Daltons) and the $^{13}C_6$-monochlorobiphenyl surrogate (194 Daltons) in CMA-A sample No. 2110.

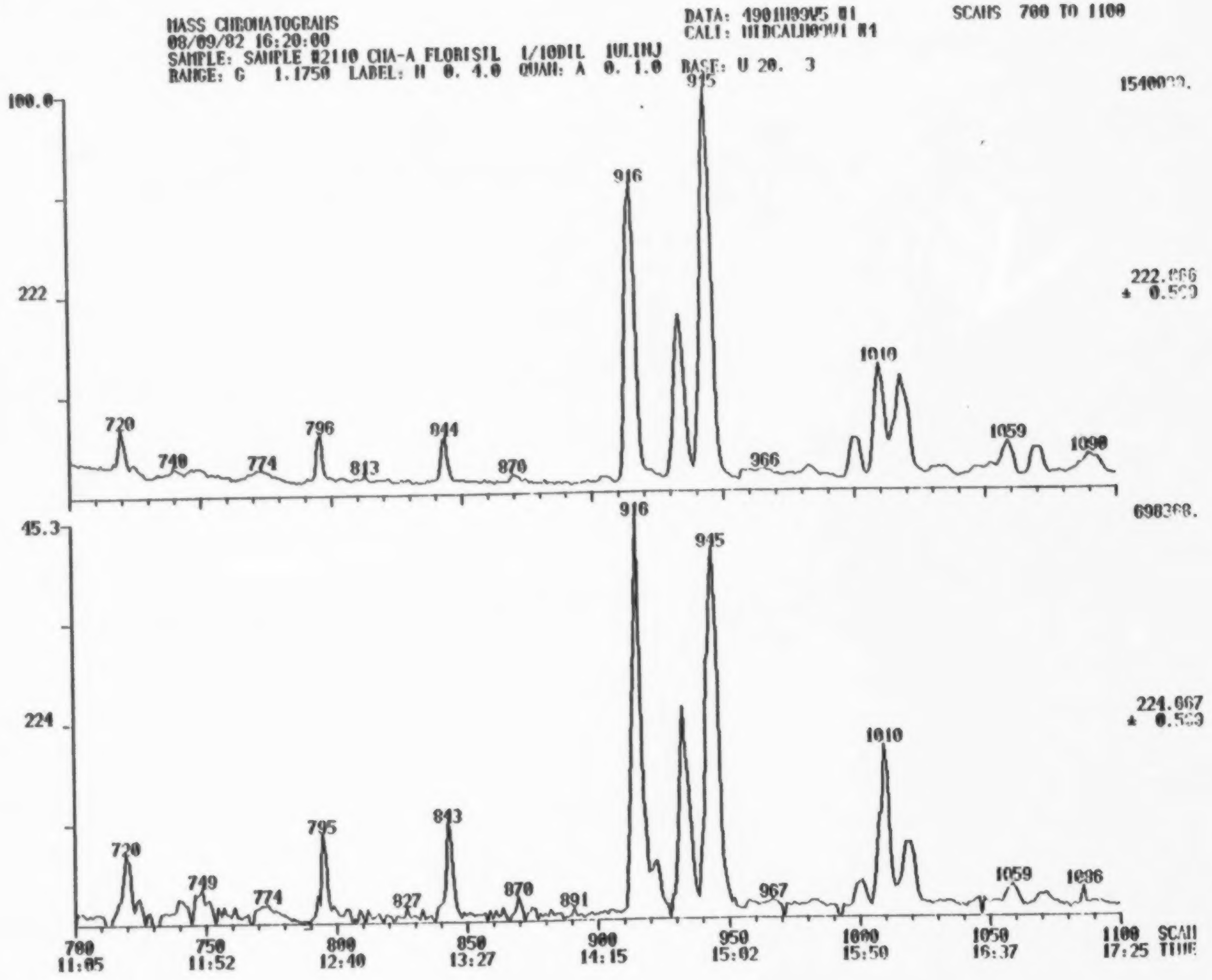
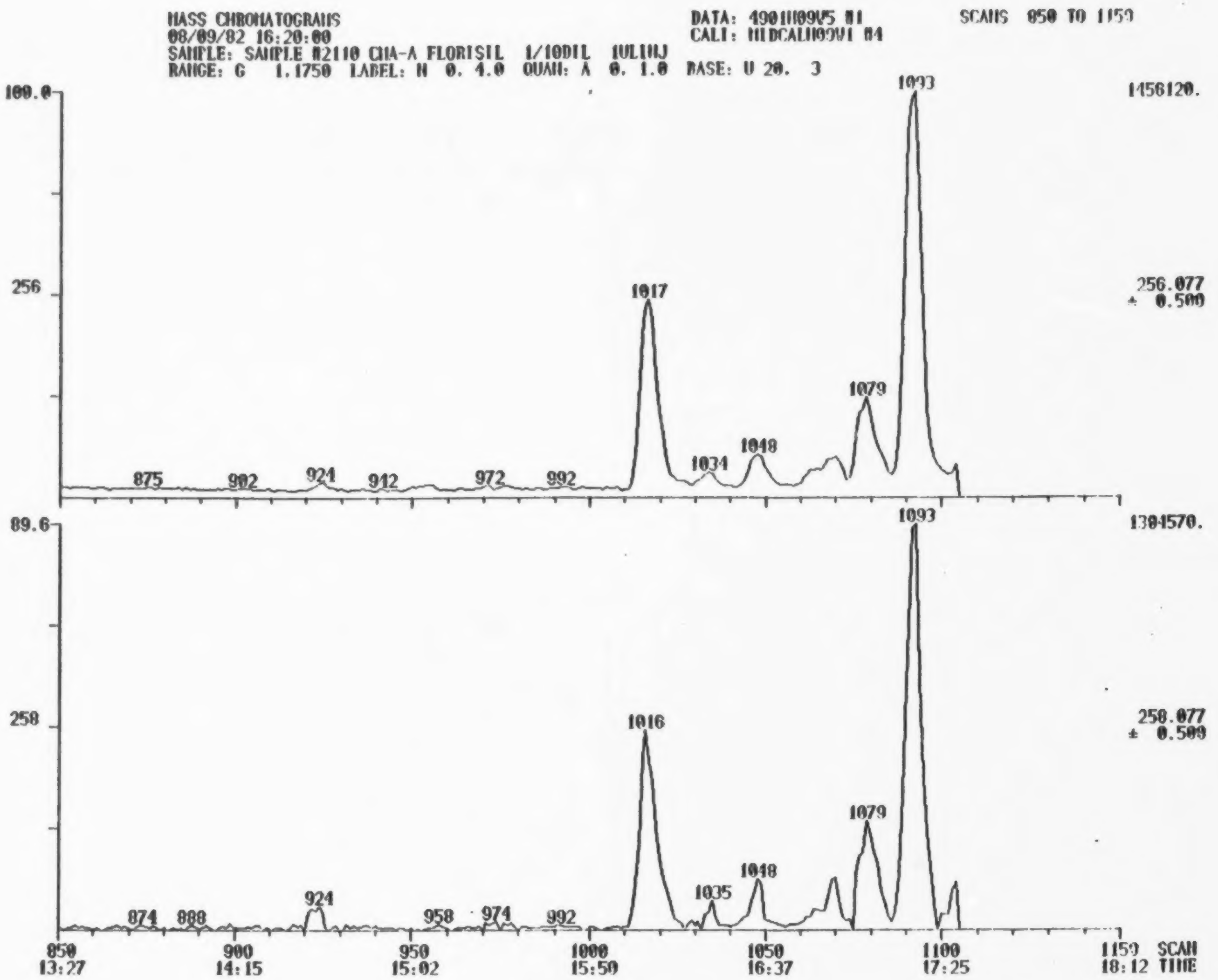


Figure 8. SIM ion plots for dichlorobiphenyls (222 and 224 Daltons) in CMA-A sample No. 2110.



```
MASS CHROMATOGRAMS                                      DATA: 4901M09V5 #1        SCANS  850 TO 1159
08/09/82 16:20:00                                       CALI: MIDCALM09V1 #4
SAMPLE: SAMPLE #2110 CMA-A FLORISIL  1/10DIL  1ULINJ
RANGE: G   1,1750  LABEL: N  0, 4.0  QUAN: A  0, 1.0  BASE: U 20,  3
```

Figure 9. SIM ion plots for trichlorobiphenyls (256 and 258 Daltons) in CMA-A sample No. 2110.

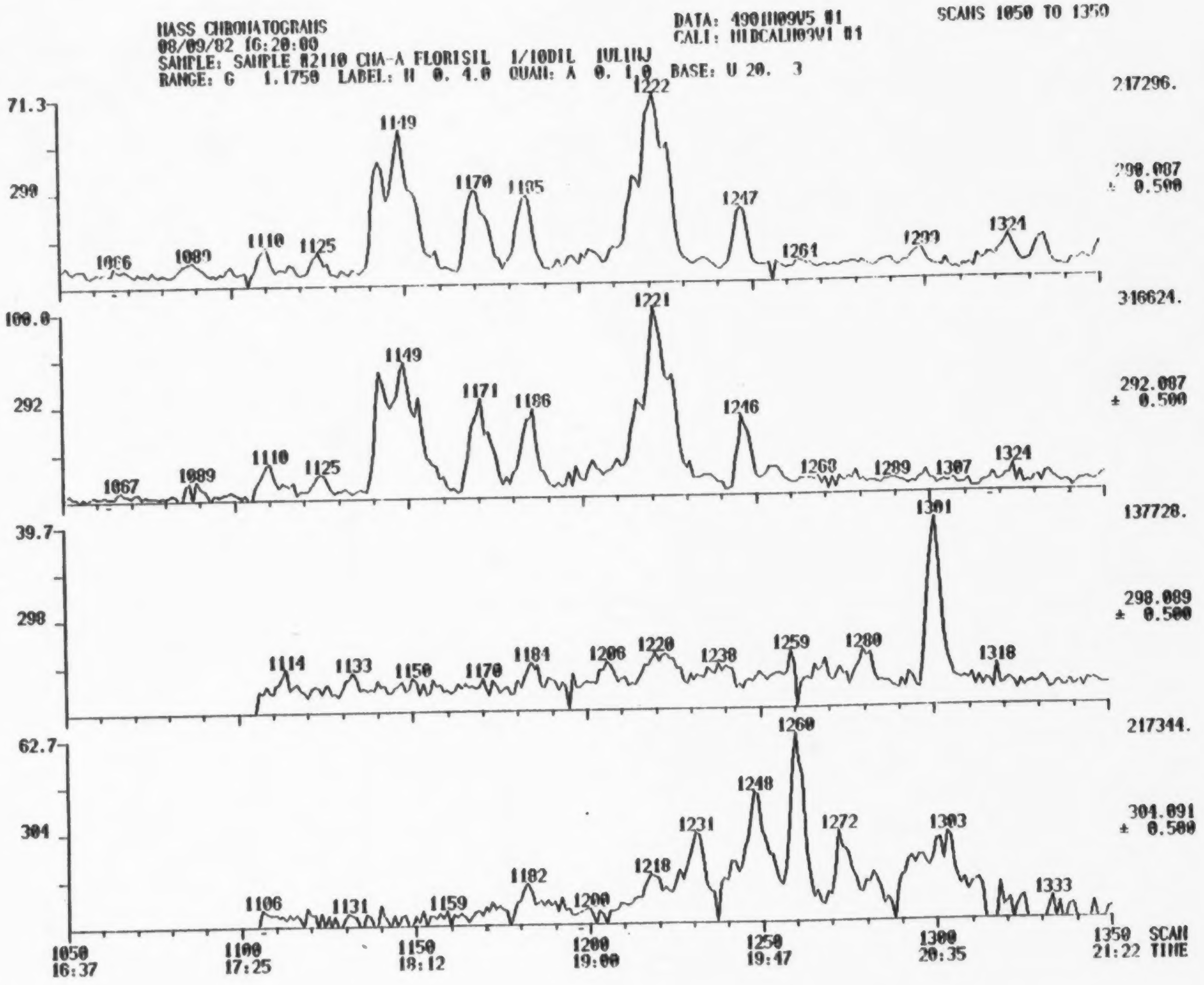


Figure 10. SIM ion plots for tetrachlorobiphenyls (290 and 292 Daltons), 3,3',4,4'-tetrachlorobiphenyl-d_6 (298 Daltons), and the $^{13}C_{12}$-tetrachlorobiphenyl surrogate (304 Daltons) in CMA-A sample No. 2110.

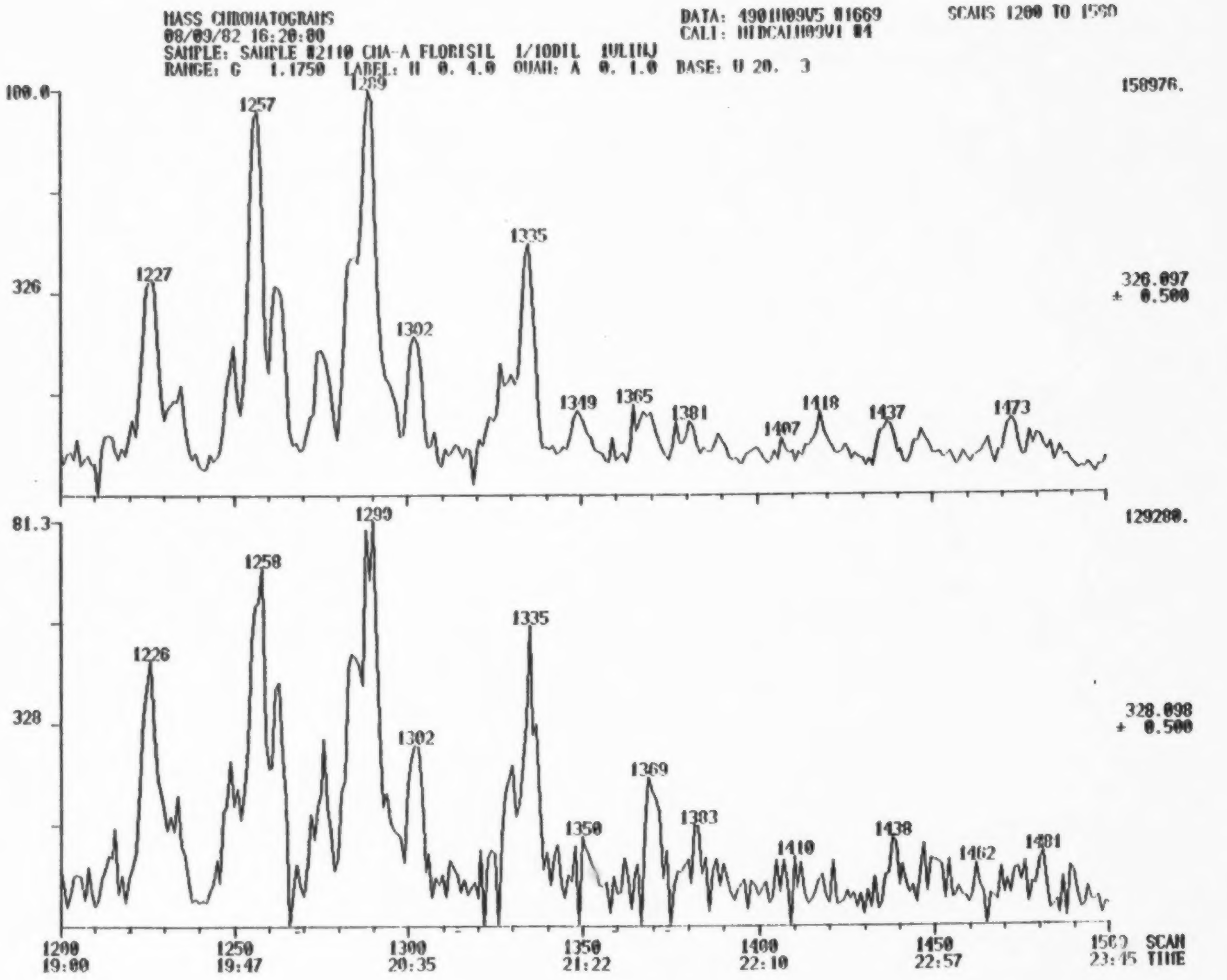


Figure 11. SIM ion plots for pentachlorobiphenyls (326 and 328 Daltons) in CMA-A sample No. 2110.

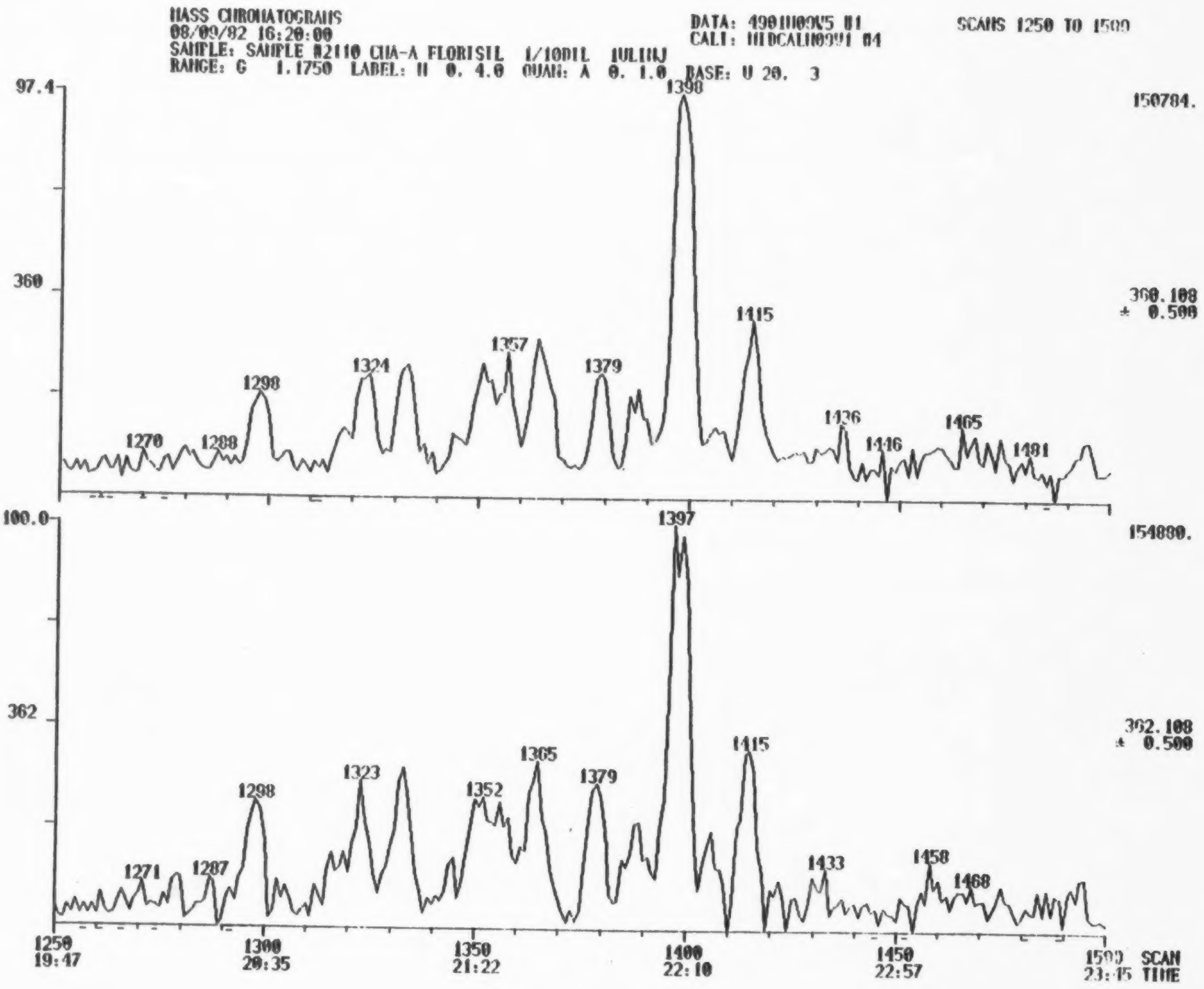


Figure 12. SIM ion plots of hexachlorobiphenyls (360 and 362 Daltons) in CMA-A sample No. 2110.

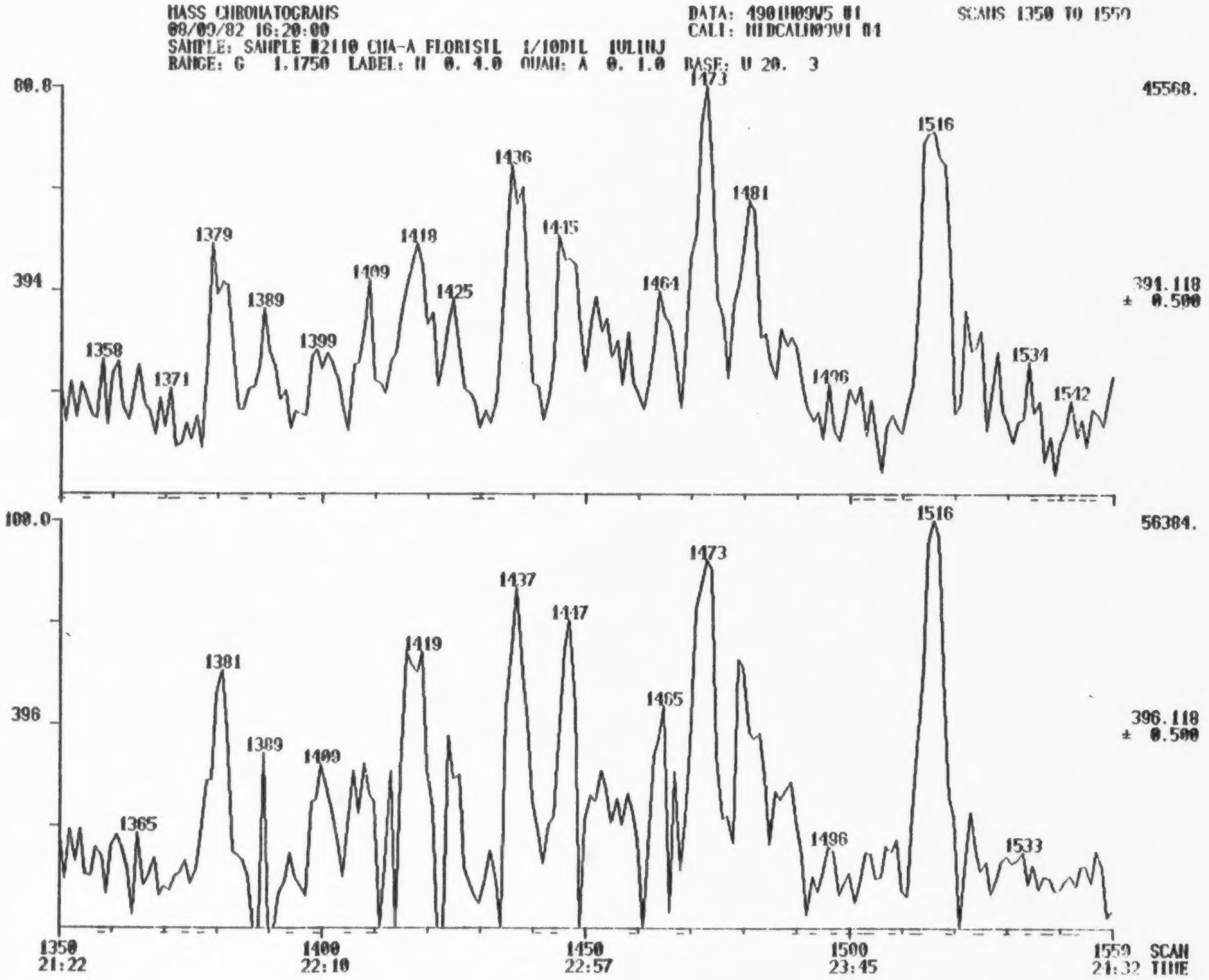


Figure 13. SIM ion plots of heptachlorobiphenyls (394 and 396 Daltons) in CMA-A sample No. 2110.

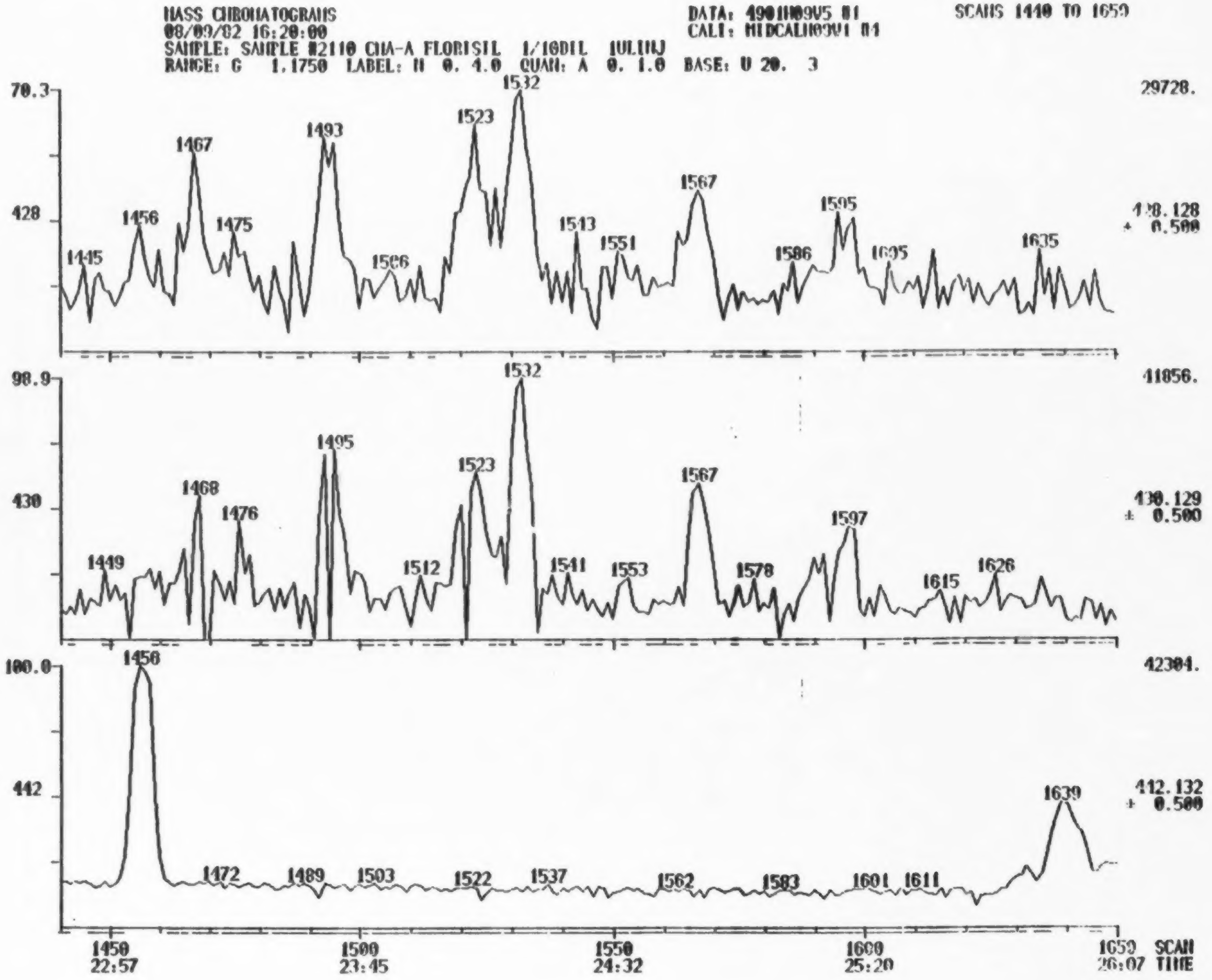


Figure 14. SIM ion plots of octachlorobiphenyls (428 and 430 Daltons) and the $^{13}C_{12}$-octachlorobiphenyl surrogate (442 Daltons) in CMA-A sample No. 2110.

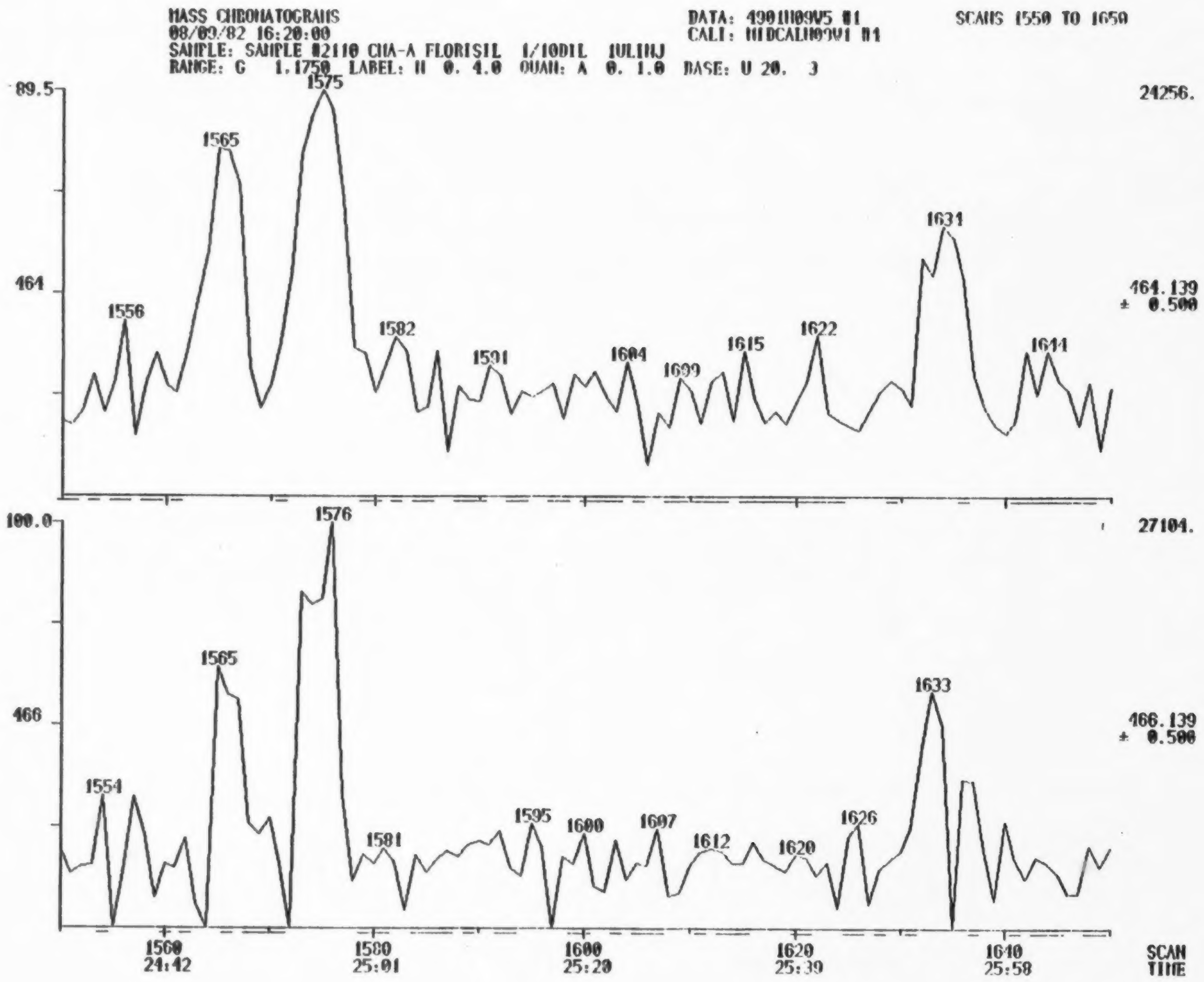


Figure 15. SIM ion plots of nonachlorobiphenyl (464 and 466 Daltons) in CMA-A sample No. 2110.

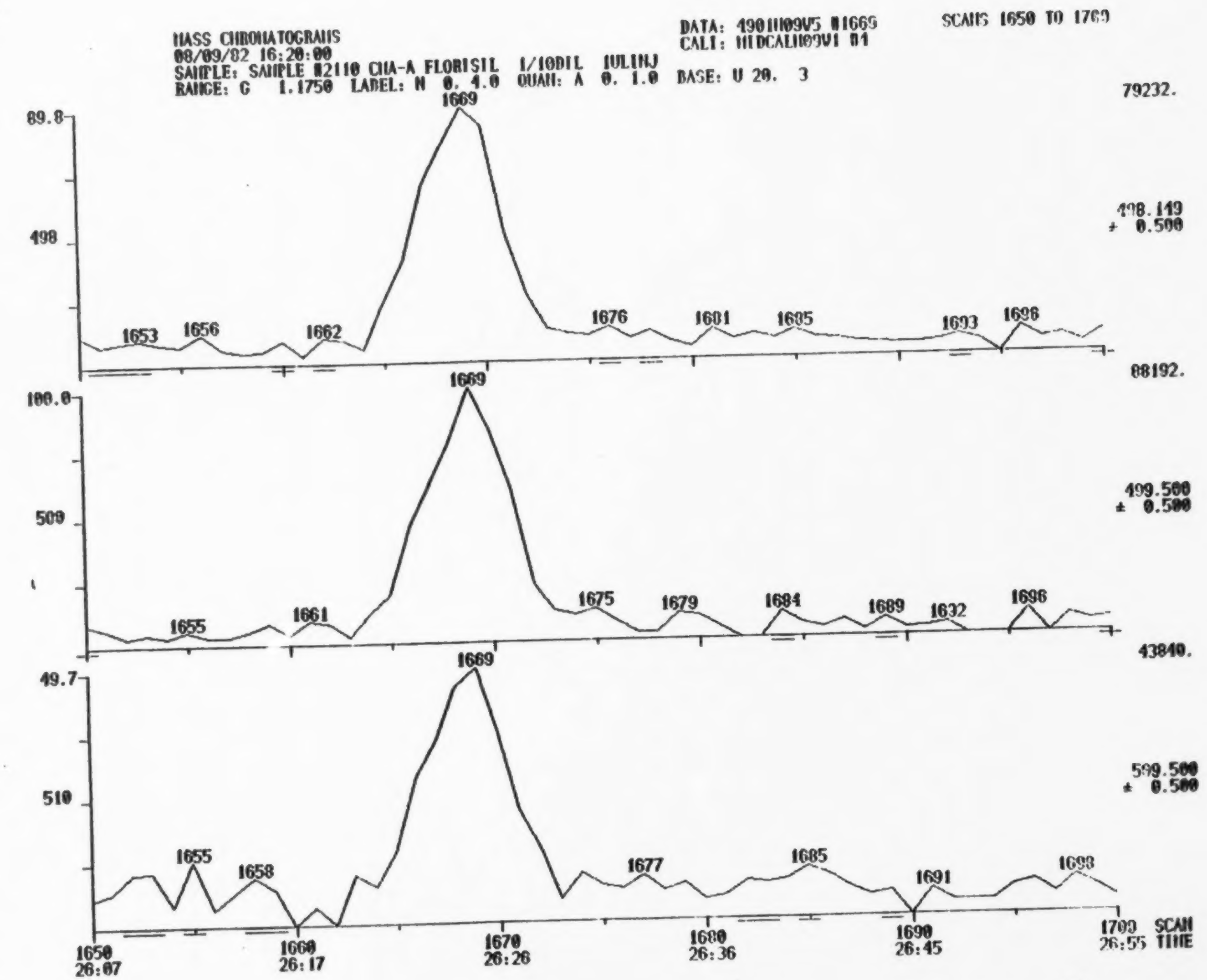


Figure 16. SIM ion plots of decachlorobiphenyl (498 and 500 Daltons) and the $^{13}C_{12}$-decachlorobiphenyl (510 Daltons) in CMA-A sample No. 2110.

SECTION 5

REFERENCES

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USEPA. 1979b (December 3). U.S. Environmental Protection Agency. Organochlorine pesticides and PCBs--method 608. 44 FR 69501.

USEPA. 1982 (June 8). U.S. Environmental Protection Agency. Polychlorinated biphenyls (PCBs); manufacture, processing, distribution, and use in closed and controlled waste manufacturing processes. FR 74 24976.

APPENDIX A

SUPPLEMENTARY GC/EIMS DATA ON PCB CONGENERS

The following data support the method validation section for gas chromatography/electron impact mass spectrometry (GC/EIMS) of polychlorinated biphenyls (PCB). Table A-1 lists the average relative response factors (RRF) for the 77 commercially available PCB congeners determined as four replicates. Table A-2 presents results of the Student's t-test used to determine the significance of differences for average RRFs for PCB homologs measured on a single day versus multiple days. The data in Table A-2 indicate that only the average RRFs for the heptachlorobiphenyl homolog are significantly different.

Table A-3 presents the results of the Student's t-test used to determine the significance of differences for the average RRFs for the PCB homologs determined with the quadrupole and magnetic sector mass spectrometers. All 77 PCB congeners were determined in a single day for each of the instrument studies. This comparison indicates that the average RRF values are significantly different, which was expected. However, the relative standard deviations are not significantly different, indicating that the selection of the calibration standards is appropriate. These conclusions are discussed more fully in the text.

Table A-4 presents results of the Student's t-test used to determine significance of differences for the RRFs for the 11 congeners in Solution No. 1, which was analyzed daily. An example of the data generated for multiple analysis of Solution No. 1 is presented in Figures 1 to 23. This information includes a capillary GC/EIMS chromatogram of Solution No. 1, the mass spectra of each component in this solution, and a graphic illustration of the distribution of several measurements of each congener about the average response factor. It should be noted that the standard deviation and relative standard deviation presented in these plots are different from that reported in the text due to calculation of the standard deviation using N weighting rather than the correct N-1 weighting. All other standard deviations reported in this document are based on the N-1 weighting.

The relative retention times of the 77 PCB congeners with respect to 3,3',4,4'-tetrachlorobiphenyl-d_6 determined with the Finnigan 4023 quadrupole and the Varian MAT 311A mass spectrometers are presented in Table A-5. A relative retention time unit of 0.01 (10 sec) is required for resolution of two specific congeners based on the gas chromatography parameters used to generate these numbers.

TABLE A-1. RELATIVE RESPONSE FACTORS FOR COMMERCIALLY AVAILABLE PCB CONGENERS (QUADRUPOLE)

Congener no.	Degree of chlorination	Average relative response factor[a]	Standard deviation	Coefficient of variation (%)
1	1	4.073	0.118	2.905
2	1	2.951	0.056	1.894
3	1	2.969	0.028	0.956
4	2	1.232	0.008	0.646
5	2	1.959	0.035	1.803
7	2	2.008	0.027	1.366
8	2	2.049	0.023	1.134
9	2	2.148	0.061	2.846
10	2	1.880	0.031	1.658
11	2	3.073	0.073	2.363
12	2	1.929	0.036	1.877
14	2	2.083	0.098	4.702
15	2	1.909	0.089	4.686
18	3	1.104	0.012	1.089
21	3	1.586	0.018	1.110
24	3	1.051	0.033	3.105
26	3	1.714	0.013	0.731
28	3	1.587	0.028	1.733
29	3	2.195	0.048	2.188
30	3	1.526	0.067	4.418
31	3	1.706	0.024	1.409
33	3	1.688	0.031	1.863
40	4	0.597	0.013	2.152
44	4	0.712	0.007	0.946
47	4	1.062	0.059	5.591
49	4	0.831	0.019	2.245
50	4	0.957	0.025	2.574
52	4	0.732	0.011	1.504
53	4	0.750	0.008	1.006
54	4	0.958	0.013	1.344
61	4	0.975	0.069	7.094
65	4	1.086	0.022	1.994
66	4	1.139	0.068	5.966
69	4	1.058	0.012	1.110
70	4	1.091	0.050	4.548
72	4	0.980	0.048	4.870
75	4	1.185	0.061	5.113
77	4	1.095	0.050	4.595

(continued)

TABLE A-1 (continued)

Congener no.	Degree of chlorination	Average relative response factor[a]	Standard deviation	Coefficient of variation (%)
87	5	0.617	0.011	1.710
88	5	0.611	0.005	0.744
93	5	0.574	0.010	1.677
97	5	0.719	0.008	1.139
100	5	0.727	0.003	0.428
101	5	0.653	0.004	0.538
103	5	0.566	0.009	1.627
104	5	0.824	0.025	3.048
115	5	0.853	0.061	7.146
116	5	0.785	0.013	1.654
119	5	0.762	0.022	2.911
121	5	0.948	0.020	2.127
128	6	0.499	0.005	1.093
129	6	0.431	0.004	0.813
136	6	0.689	0.016	2.336
137	6	0.533	0.008	1.582
138	6	0.433	0.008	1.946
139	6	0.462	0.026	5.686
141	6	0.419	0.010	2.353
143	6	0.490	0.005	0.986
151	6	0.473	0.013	2.826
153	6	0.549	0.050	9.101
154	6	0.221	0.001	0.570
154	6	0.511	0.010	2.039
155	6	0.587	0.011	1.828
156	6	0.599	0.044	7.431
171	7	0.346	0.002	0.640
181	7	0.383	0.009	2.379
183	7	0.380	0.010	2.501
185	7	0.336	0.006	1.729
195	8	0.263	0.003	1.184
198	8	0.262	0.008	2.887
200	8	0.301	0.007	2.392
202	8	0.250	0.007	2.663
204	8	0.221	0.007	3.200
206	9	0.193	0.003	1.723
207	9	0.237	0.008	3.547
208	9	0.259	0.003	1.315
209	10	0.213	0.006	2.837

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[a] Relative to 3,3',4,4'-tetrachlorobiphenyl-d_6. All relative response factors were calculated as the average of four replicate measurements made on the same day.

TABLE A-2. STUDENT'S TWO-SIDED t-TEST TO DETERMINE SIGNIFICANT DIFFERENCES BETWEEN QUADRUPOLE RESPONSE FACTORS CALCULATED ON THE SAME DAY VERSUS MULTIPLE DAYS

PCB homolog	Number of isomers	Average RRF from replicate measurements[a]	Standard deviation	Average RRF from single measurement[b]	Standard deviation	t-Statistic	Significant at 95% level?
Monochloro-	3	3.331	0.643	2.739	0.254	1.478	No
Dichloro-	10	2.027	0.447	2.048	0.322	-0.119	No
Trichloro-	9	1.573	0.341	1.592	0.289	-0.131	No
Tetrachloro-	16	0.950	0.175	0.946	0.189	0.0618	No
Pentachloro-	12	0.720	0.120	0.725	0.127	-0.1085	No
Hexachloro-	13	0.513	0.078	0.500	0.096	0.377	No
Heptachloro-	4	0.361	0.024	0.308	0.025	3.119	Yes
Octachloro-	6	0.253	0.030	0.224	0.039	1.398	No
Nonachloro-	3	0.229	0.034	0.188	0.030	1.591	No
Decachloro-	1	0.213	0.006	0.179	-[c]	-[d]	-[d]

a Four replicate measurements of the RRF were made for each isomer. For example, the three monochlorobiphenyl isomers were measured four times each. Hence, the average RRF and standard deviation were calculated from 12 distinct values.

b A single measurement for each of the 77 PCB congeners was completed in a single day. Hence, the average RRF reported is the average of one measured RRF for each isomer within a homolog. For example, the average RRF and standard deviation reported for the monochlorobiphenyl was calculated from three distinct values.

c Single measurement.

d Cannot test significance of difference between single measurements.

TABLE A-3. COMPARISON OF THE AVERAGE RELATIVE RESPONSE FACTORS ($\overline{RRF}$) DETERMINED WITH QUADRUPOLE (FINNIGAN 4023) AND MAGNETIC SECTOR (VARIAN MAT 311A) MASS SPECTROMETERS[a]

PCB homolog	Number of isomers	Finnigan 4023 quadrupole MS		Varian MAT 311A magnetic sector MS		$\overline{RRF}$s significantly different at the 95% confidence level[b]	Variances significantly different at the 95% confidence level[c]
		$\overline{RRF}$	Standard deviation	$\overline{RRF}$	Standard deviation		
Monochloro-	3	2.739	0.250	2.329	0.199	No	No
Dichloro-	10	2.038	0.32	1.663	0.229	Yes	No
Trichloro-	9	1.592	0.29	1.167	0.248	Yes	No
Tetrachloro-	16	0.946	0.19	0.902	0.130	No	No
Pentachloro-	12	0.725	0.13	0.780	0.136	No	No
Hexachloro-	13	0.500	0.10	0.640	0.124	Yes	No
Heptachloro-	4	0.308	0.025	0.497	0.060	Yes	No
Octachloro-	6	0.224	0.04	0.463	0.071	Yes	No
Nonachloro-	3	0.188	0.03	0.467	0.105	Yes	No
Decachloro-	1	0.179	-[d]	0.586	-[d]	-[e]	-[e]

a The $\overline{RRF}$ and standard deviation reported in this table for the quadrupole and magnetic sector mass spectrometers were determined as single measurements of all congeners in a single day with each instrument.

b Student's two-sided t-test was used to determine significant differences of the $\overline{RRF}$s.

c An F-test was used to determine significant differences of the standard deviations, where $F = (\text{std dev}_1)^2/(\text{std dev}_2)^2$ with (n-1, n-1) degrees of freedom.

d Single measurement.

e Cannot test significance of difference between single measurements.

TABLE A-4. STUDENT'S TWO-SIDED t-TEST TO DETERMINE SIGNIFICANT DIFFERENCES OF THE AVERAGE RELATIVE RESPONSE FACTOR ($\overline{\text{RRF}}$) FOR SOLUTION NO. 1 FOR REPLICATE ANALYSIS ON A SINGLE DAY VERSUS SINGLE ANALYSES ON MULTIPLE DAYS

PCB congener no.	Replicate analyses on single day[a]		Single analyses on multiple days[b]		t-Statistic	Significant differences of $\overline{\text{RRF}}$ at 95% confidence limit?
	$\overline{\text{RRF}}$	Standard deviation	$\overline{\text{RRF}}$	Standard deviation		
1	4.073	0.118	3.241	0.201	7.468	Yes
11	3.073	0.073	2.538	0.161	6.204	Yes
29	2.195	0.048	1.899	0.100	5.483	Yes
47	1.062	0.059	1.015	0.059	1.268	No
121	0.948	0.020	0.959	0.043	-0.479	No
136	0.689	0.016	0.683	0.058	0.186	No
181	0.383	0.009	0.374	0.035	0.662	No
195	0.263	0.003	0.275	0.028	-1.137	No
207	0.237	0.008	0.269	0.032	-2.479	Yes
209	0.213	0.006	0.230	0.027	-1.599	No

[a] The $\overline{\text{RRF}}$ and standard deviations were calculated from four replicate measurements completed in the same day.

[b] The $\overline{\text{RRF}}$ and standard deviatons were calculated from seven single measurements from seven different days.

TABLE A-5. RELATIVE RETENTION TIMES (RRT) OF 77 COMMERCIALLY AVAILABLE PCB CONGENERS MEASURED VERSUS 3,3'4,4'-TETRACHLOROBIPHENYL-d_6 DETERMINED WITH MAGNETIC SECTOR (VARIAN MAT 311A) AND QUADRUPOLE (FINNIGAN 4023) MASS SPECTROMETERS

PCB congener no.	RRT 311A	RRT 4023
Monochloro-		
1	0.403	0.425
2	0.481	0.490
3	0.474	0.499
Dichloro-		
4	0.518	0.536
5	0.598	0.606
7	0.559	0.579
8	0.590	0.606
9	0.563	0.577
10	0.521	0.534
11	0.649	0.660
12	0.660	0.671
14	0.616	0.628
15	0.677	0.681
Trichloro-		
18	0.665	0.678
21	0.762	0.767
24	0.685	0.694
26	0.729	0.738
28	0.745	0.753
29	0.719	0.728
30	0.641	0.653
31	0.741	0.752
33	0.760	0.769
Tetrachloro-		
40	0.870	0.875
44	0.838	0.843
47	0.814	0.819
49	0.811	0.817
50	0.746	0.751
52	0.804	0.810
53	0.763	0.773
54	0.720	0.731
61	0.898	0.898
65	0.822	0.826
66	0.905	0.908
69	0.800	0.807
70	0.880	0.904
72	0.853	0.856
75	0.816	0.821
77	1.002	1.003
Pentachloro-		
87	0.979	0.978
88	0.913	0.915
93	0.907	0.908
97	0.976	0.979
100	0.878	0.884
101	0.945	0.945
103	0.870	0.874
104	0.829	0.836
105	0.988	0.987
116	0.985	0.986
119	0.964	0.965
121	0.911	0.914
Hexachloro-		
128	1.163	1.156
129	1.128	1.127
136	0.994	0.996
137	1.118	1.115
138	1.108	1.103
139	1.037	1.038
141	1.096	1.093
143	1.050	1.051
151	1.020	1.021
153	1.074	1.073
154	1.002	1.004
155	0.929	0.931
156	1.194	1.188
Heptachloro-		
171	1.189	1.187
181	1.178	1.174
183	1.154	1.148
185	1.166	1.161
Octachloro-		
194	1.355	1.351
195	1.326	1.317
198	1.275	1.265
200	1.203	1.199
202	1.194	1.188
204	1.209	1.203

(continued)

TABLE A-5 (continued)

PCB congener no.	RRT 311A	RRT 4023	PCB congener no.	RRT 311A	RRT 4023
Nonachloro-			Decachloro-		
206	1.414	1.399	209	1.453	1.440
207	1.336	1.330			
208	1.319	1.318			

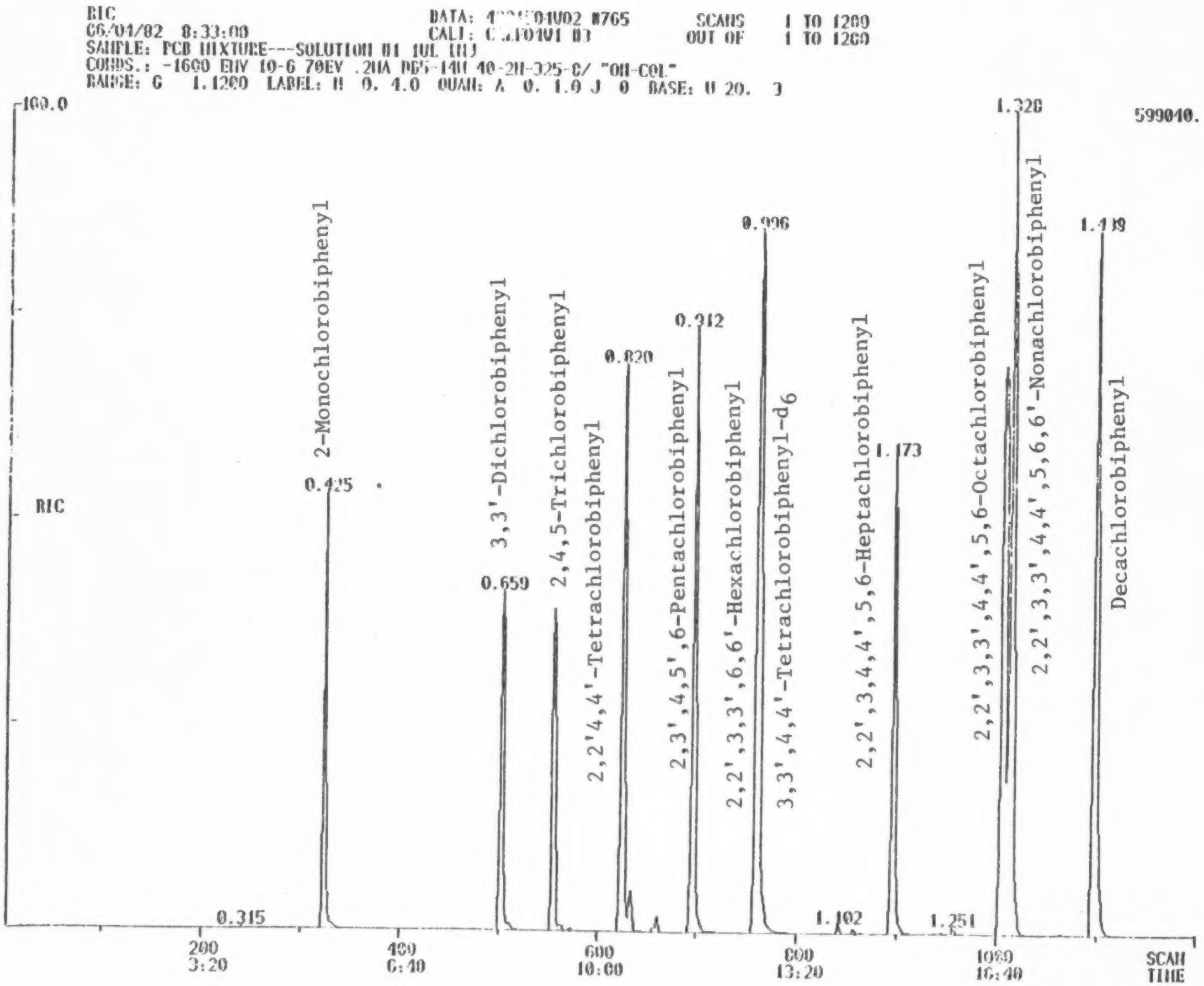
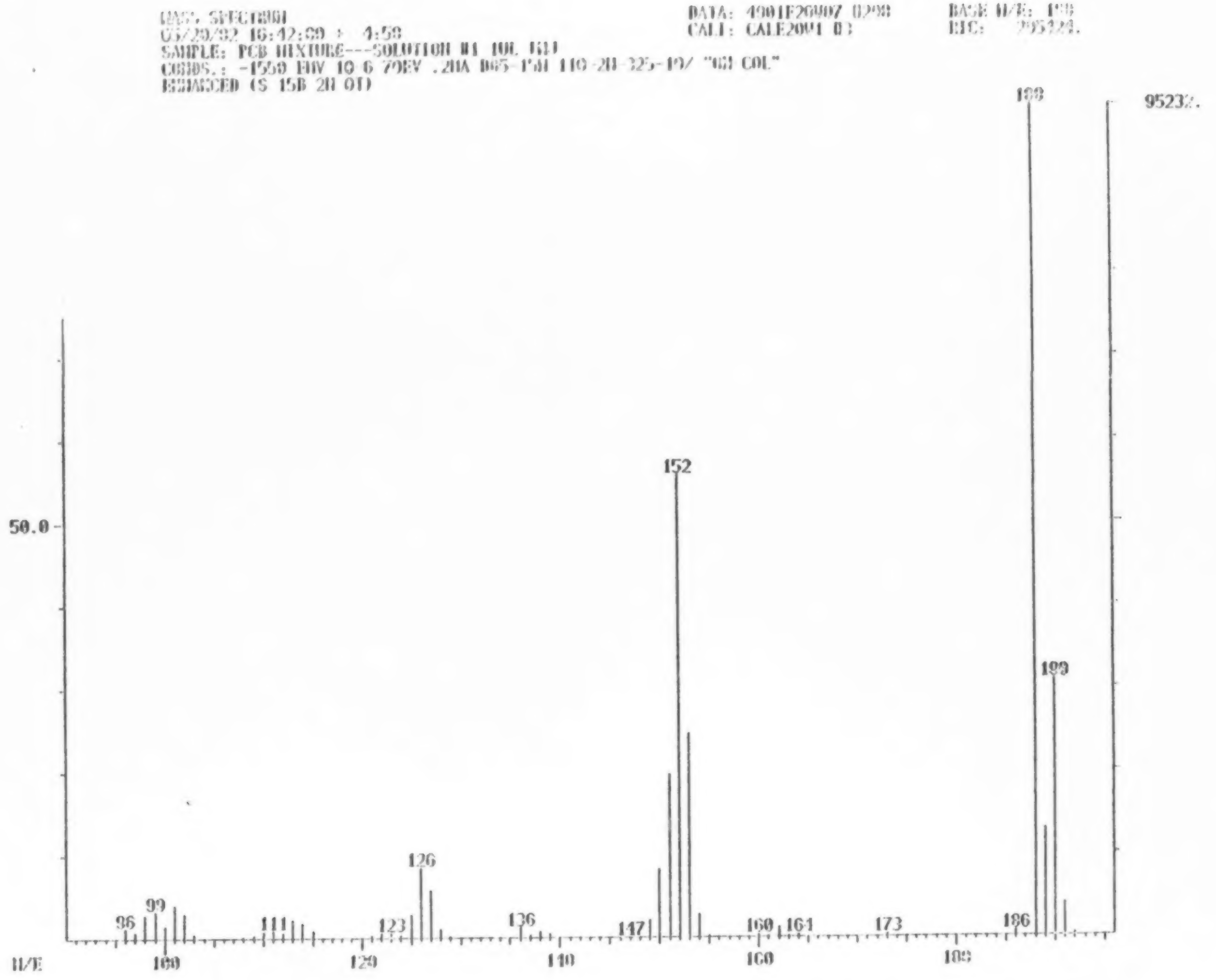


Figure A-1. Fused silica capillary gas chromatogram of PCB Solution No. 1 analyzed with electron impact mass spectrometry. Experimental conditions for separation and analysis of the PCBs are presented in the experimental section of report.



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MASS SPECTRUM                                                  DATA: 4901F26007 0298      BASE M/E: 188
05/29/82 16:42:00 + 4:58                                       CALI: CALE2001 03          RIC:   295328.
SAMPLE: PCB MIXTURE---SOLUTION #1 10L 1U
CONDS.: -1550 EMV 10 6 70EV .2MA 005-PM 110-20-325-10/ "GC COL"
ENHANCED (S 15B 2N 0T)
```

Figure A-2. Electron impact ionization mass spectrum of 2-monochlorobiphenyl.

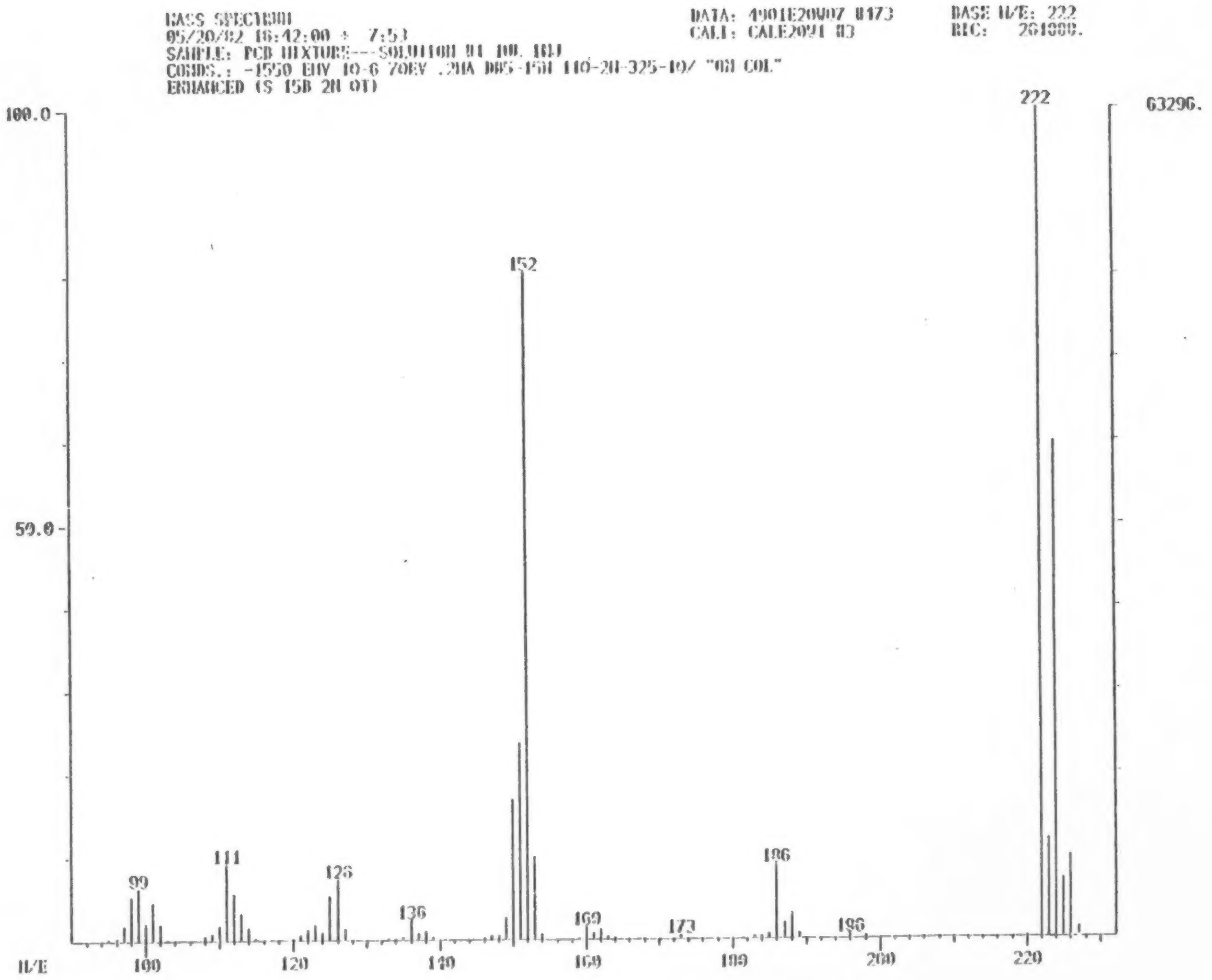

Figure A-3. Electron impact ionization mass spectrum of 3,5-dichlorobiphenyl.

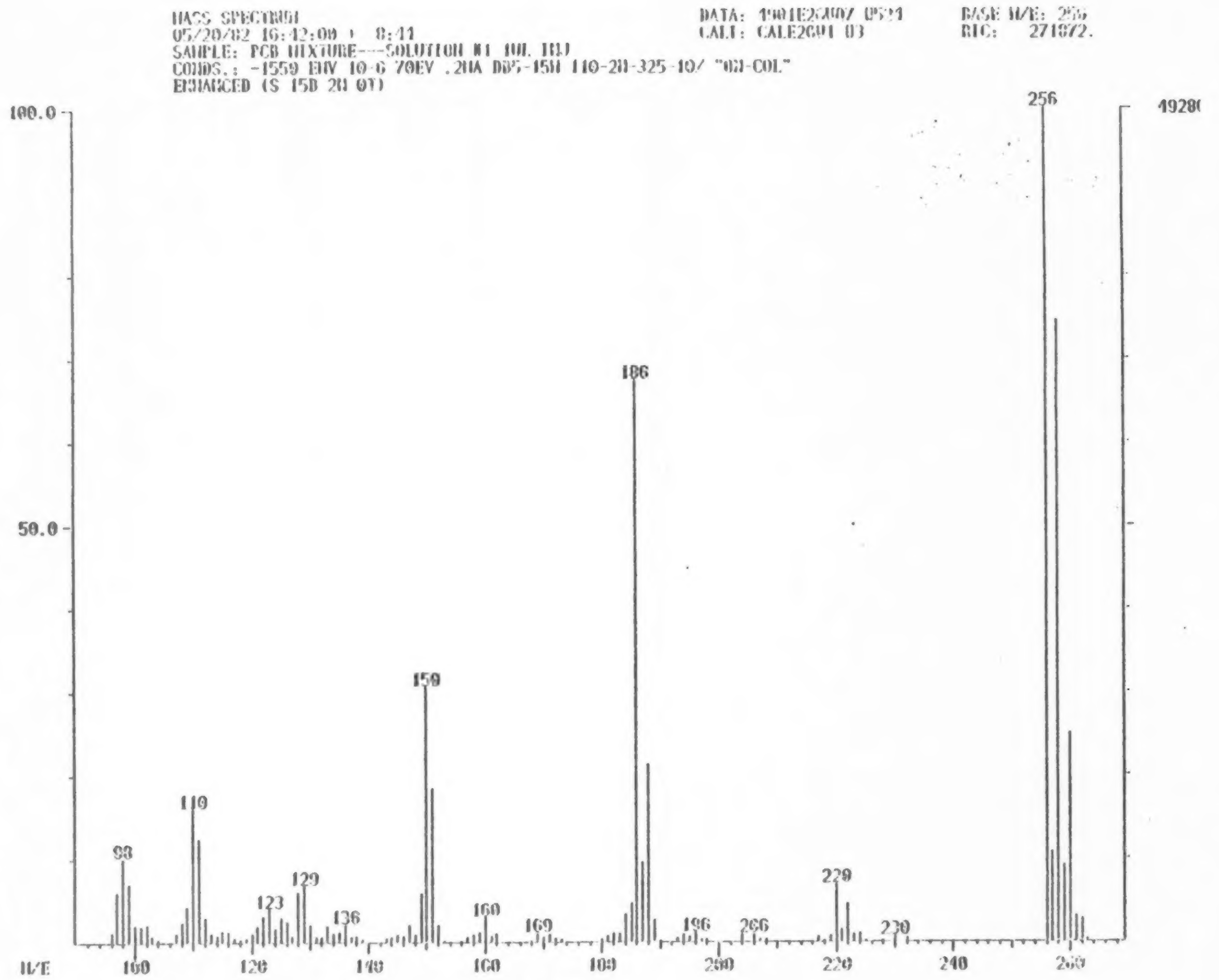

Figure A-4. Electron impact ionization mass spectrum of 2,4,5-trichlorobiphenyl.

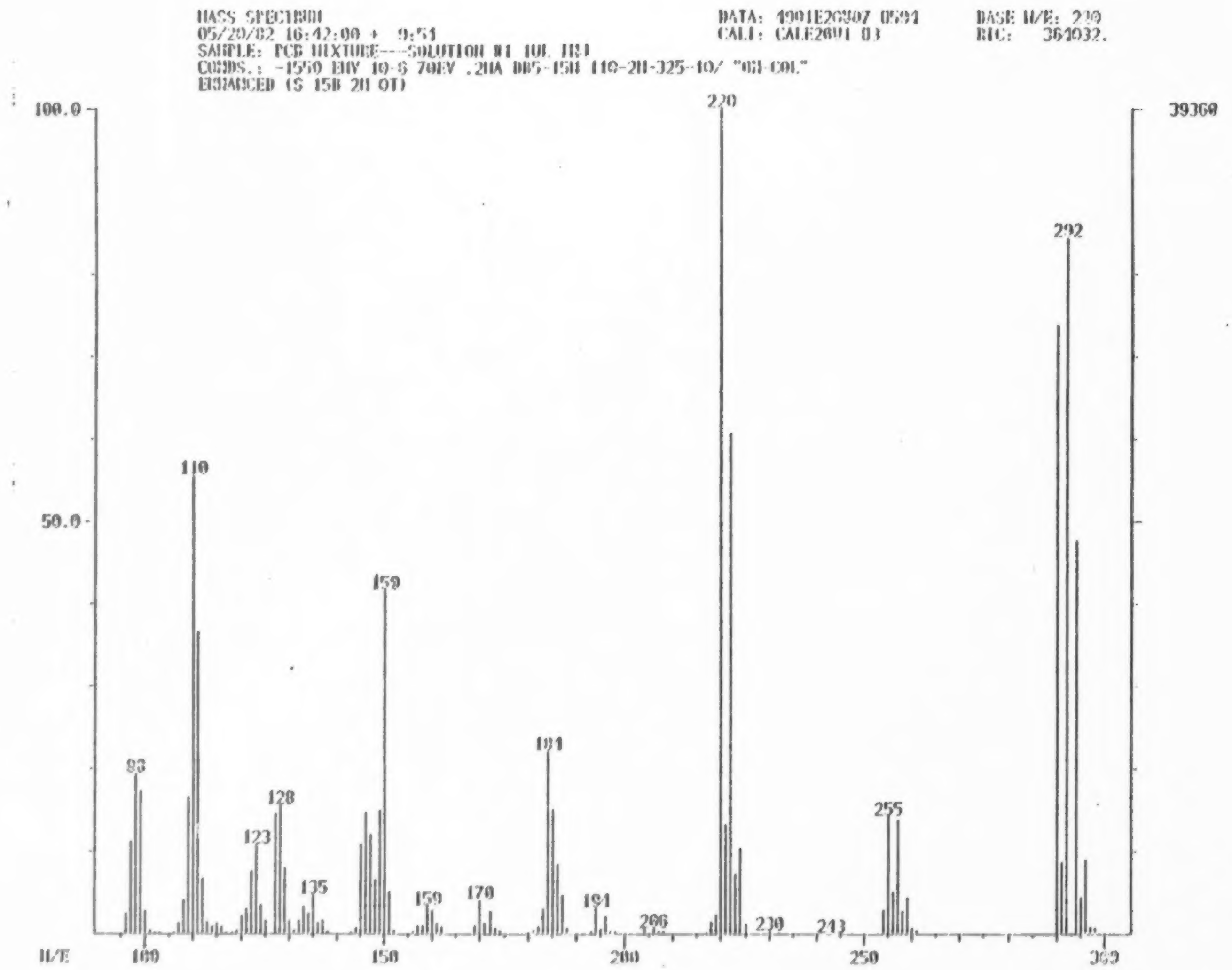

Figure A-5. Electron impact ionization mass spectrum of 2,2',4,4'-tetrachlorobiphenyl.

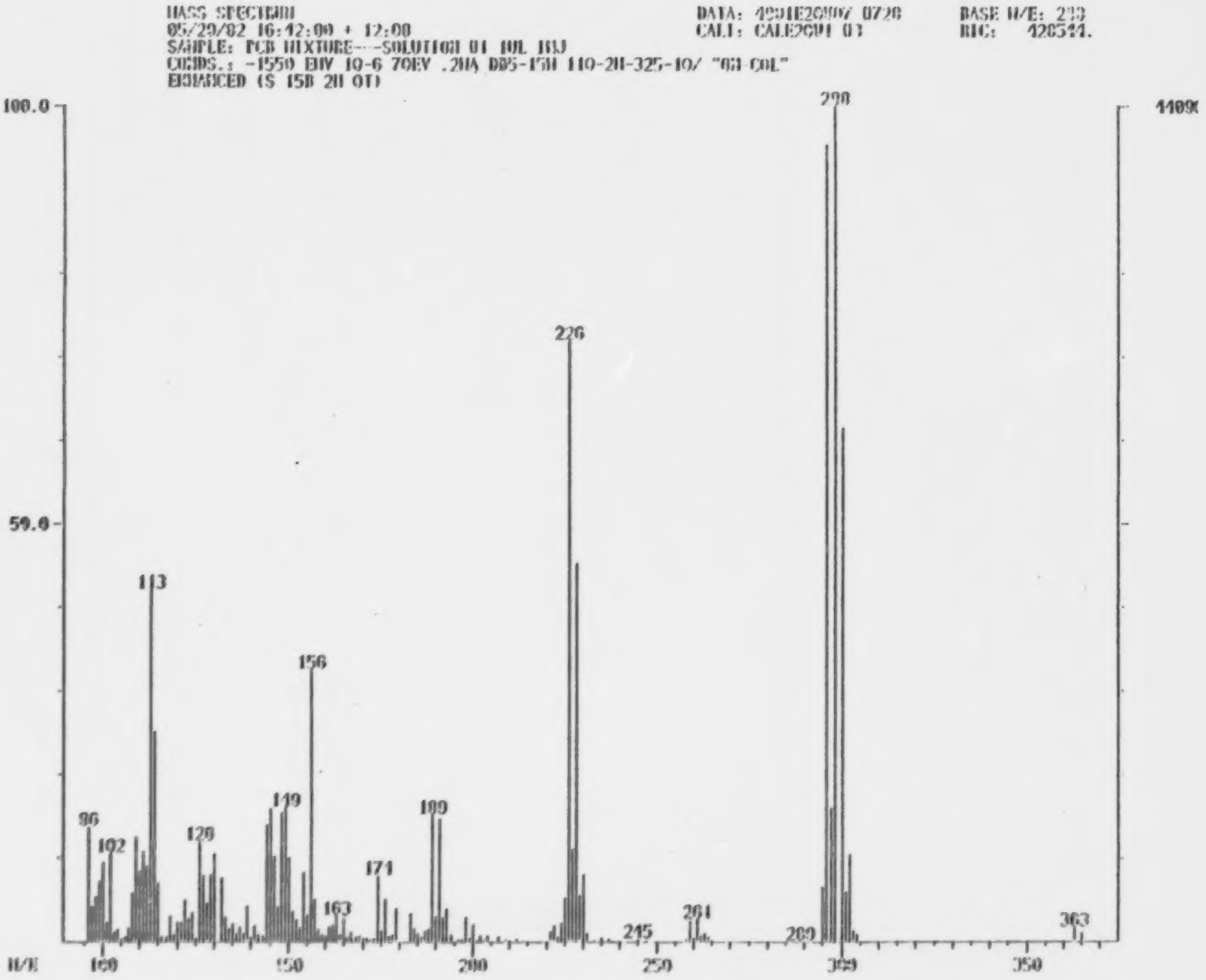

Figure A-6. Electron impact ionization mass spectrum of 3,3'4,4'-tetrachlorobiphenyl-d_6.

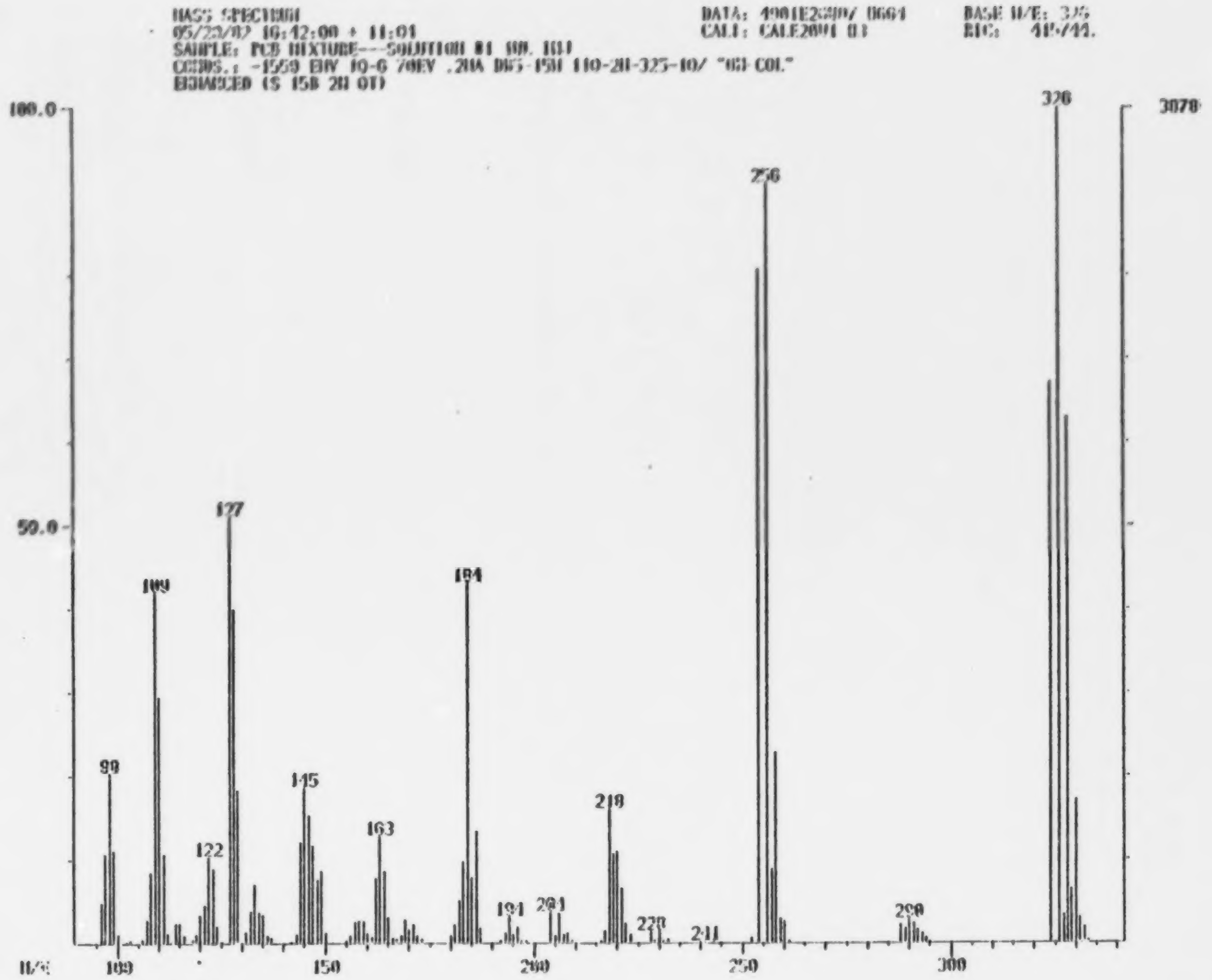

Figure A-7. Electron impact ionization mass spectrum of 2,3',4,5',6-pentachlorobiphenyl.

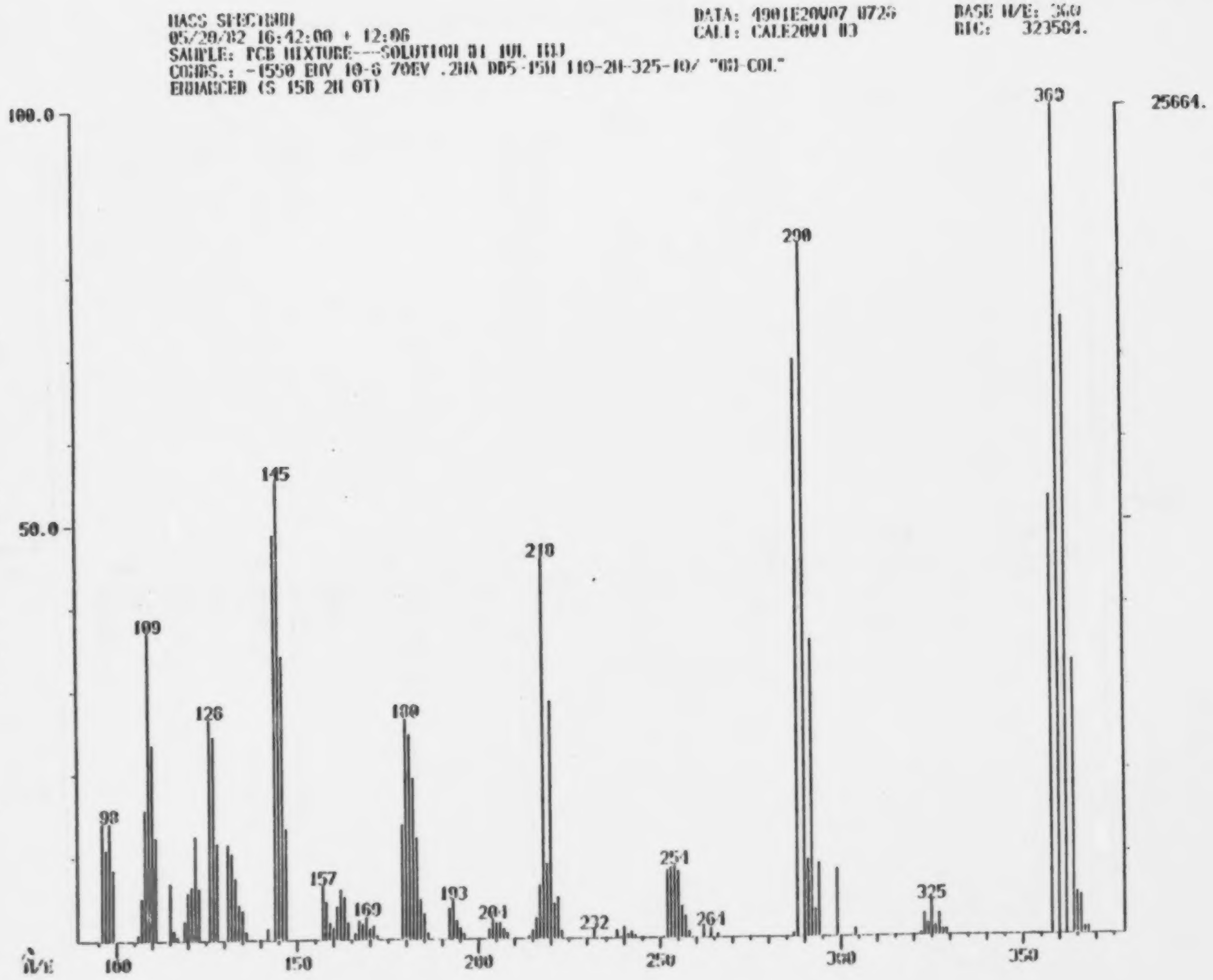

Figure A-8. Electron impact ionization mass spectrum of 2,2',3,3',6,6'-hexachlorobiphenyl.

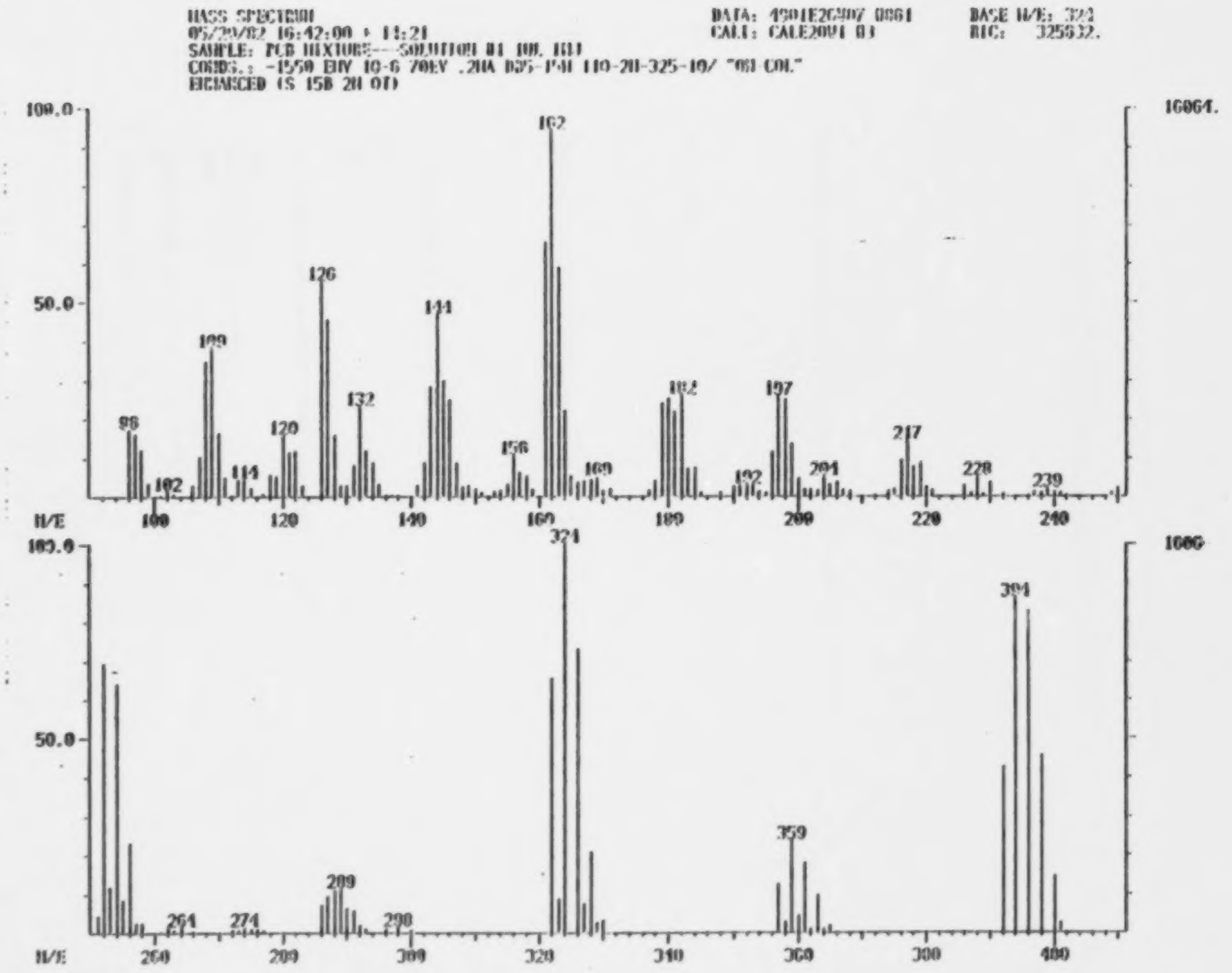

Figure A-9. Electron impact ionization mass spectrum of 2,2',3,4,4',5,6-heptachlorobiphenyl.

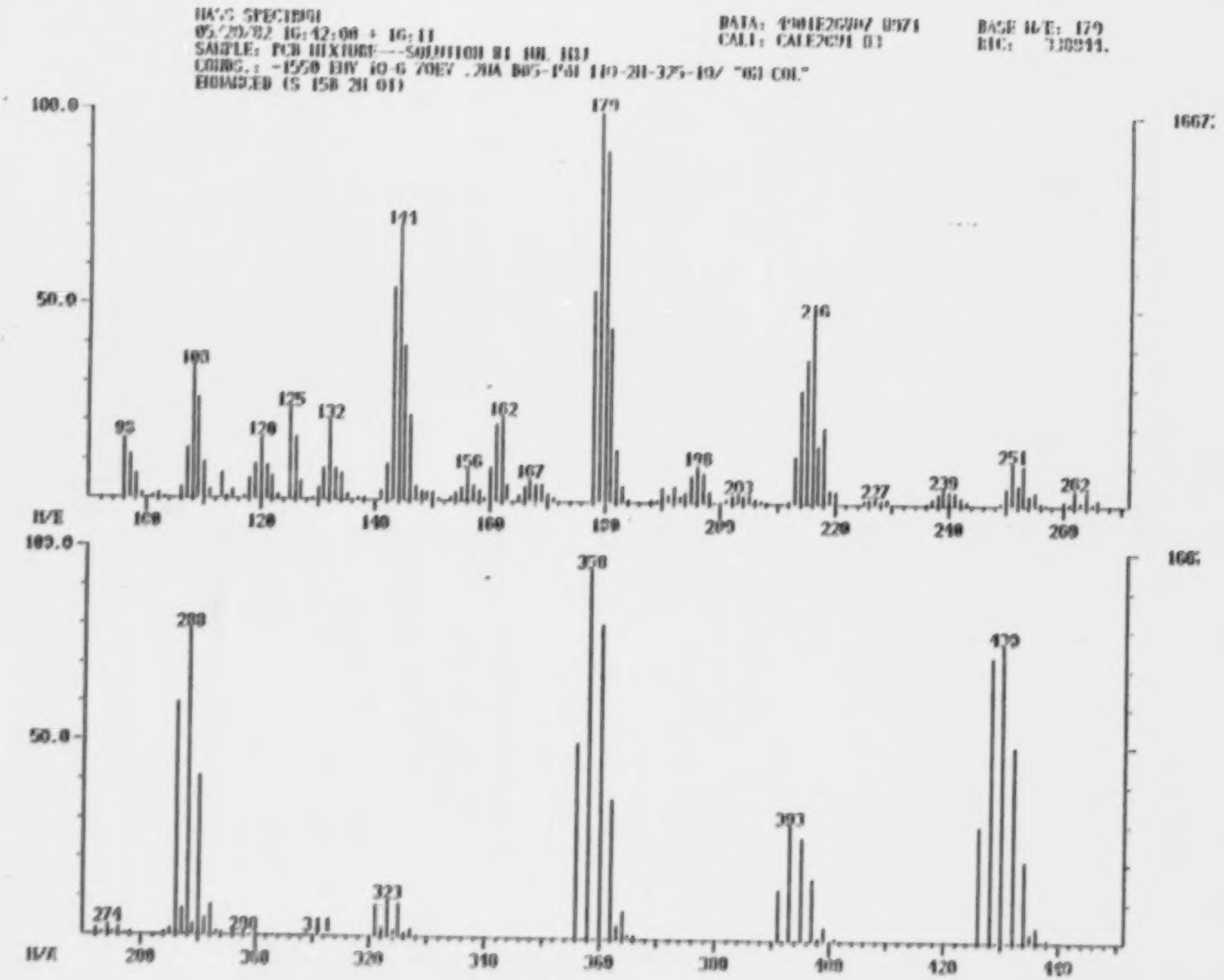

Figure A-10. Electron impact ionization mass spectrum of 2,2',3,3',4,4',5,6-octachlorobiphenyl.

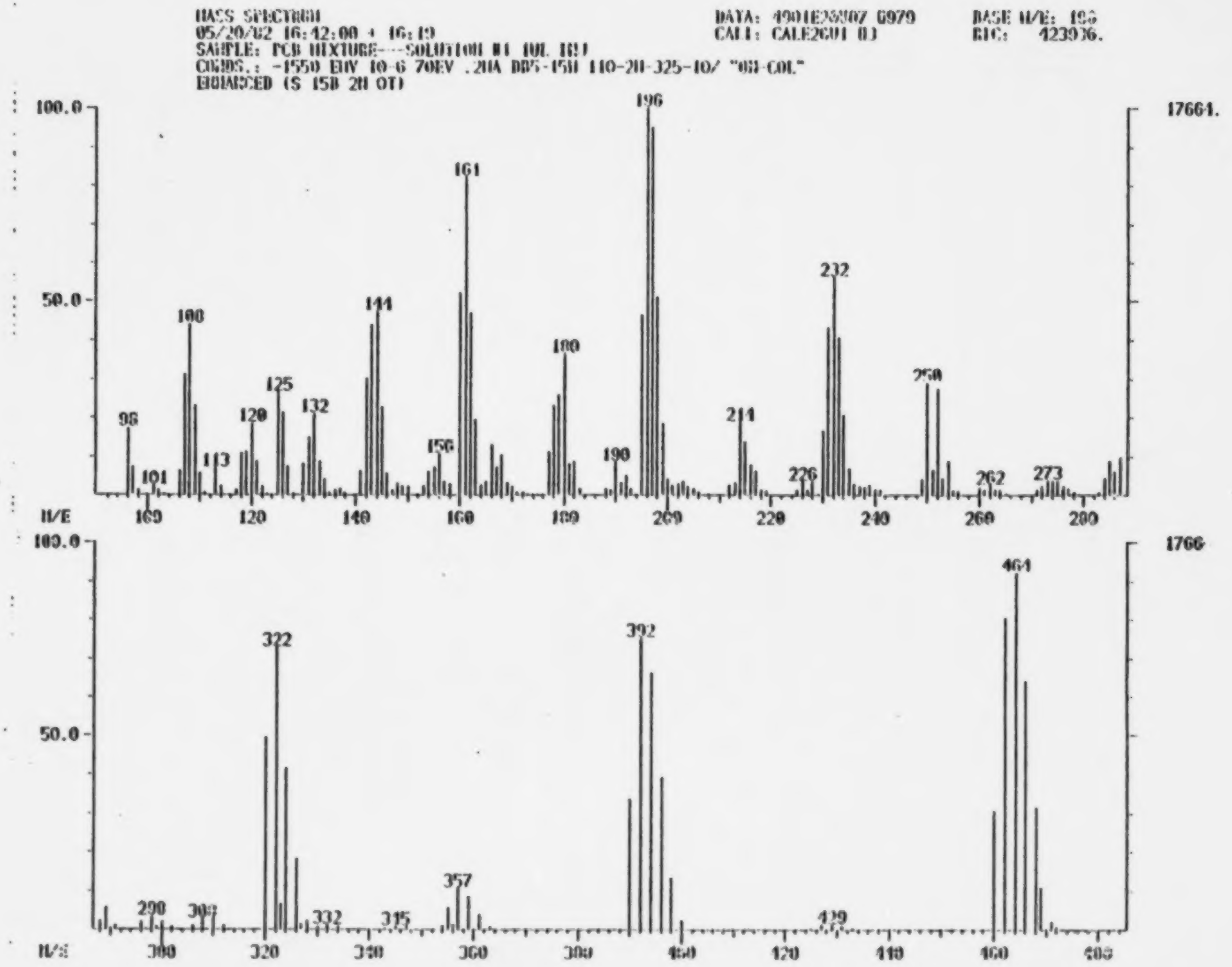

Figure A-11. Electron impact ionization mass spectrum of 2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl.

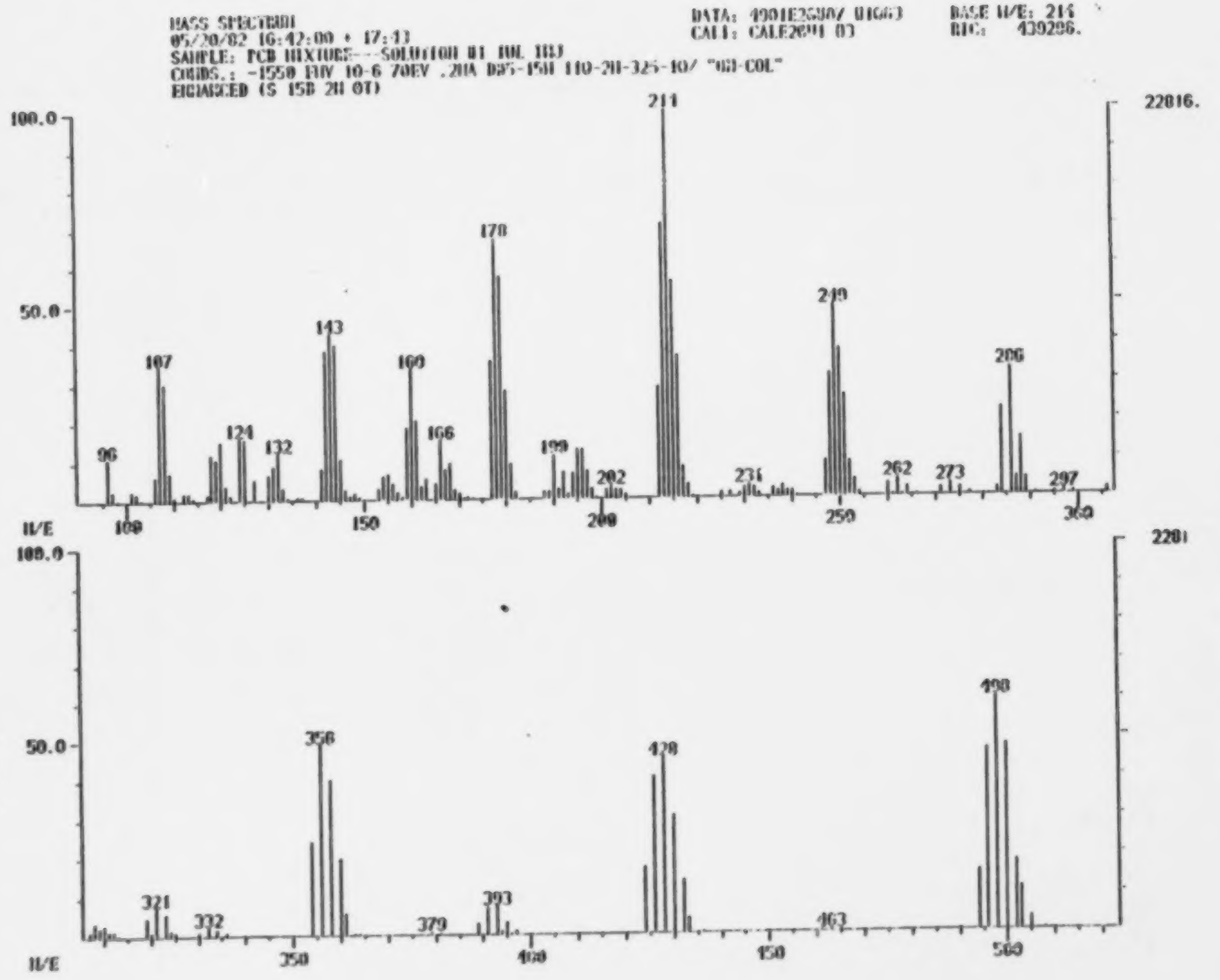

Figure A-12. Electron impact ionization mass spectrum of 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl.

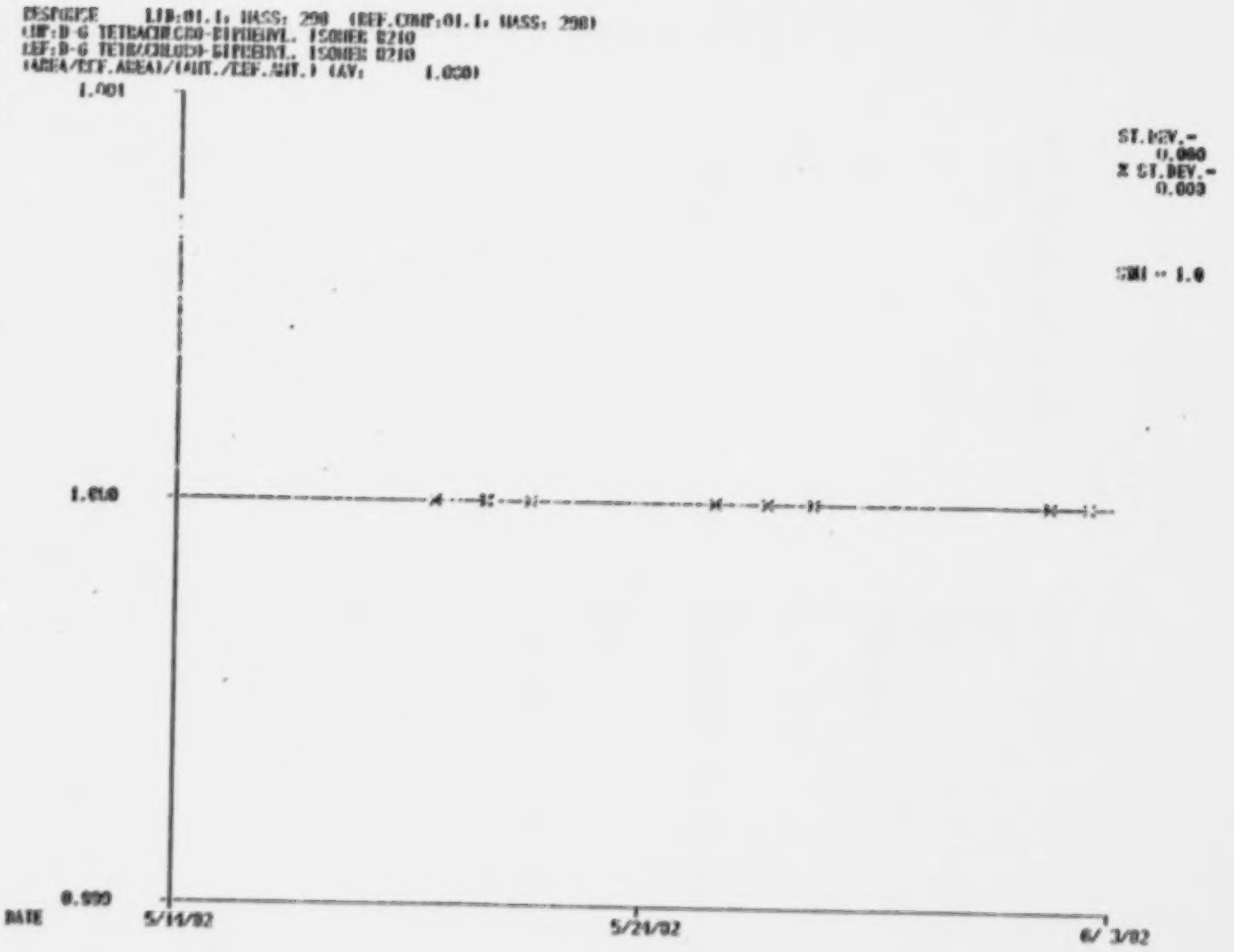

Figure A-13. Response factor plotted on a day-to-day basis for the internal standard, 3,3',4,4'-tetrachlorobiphenyl-d_6, in Solution No. 1.

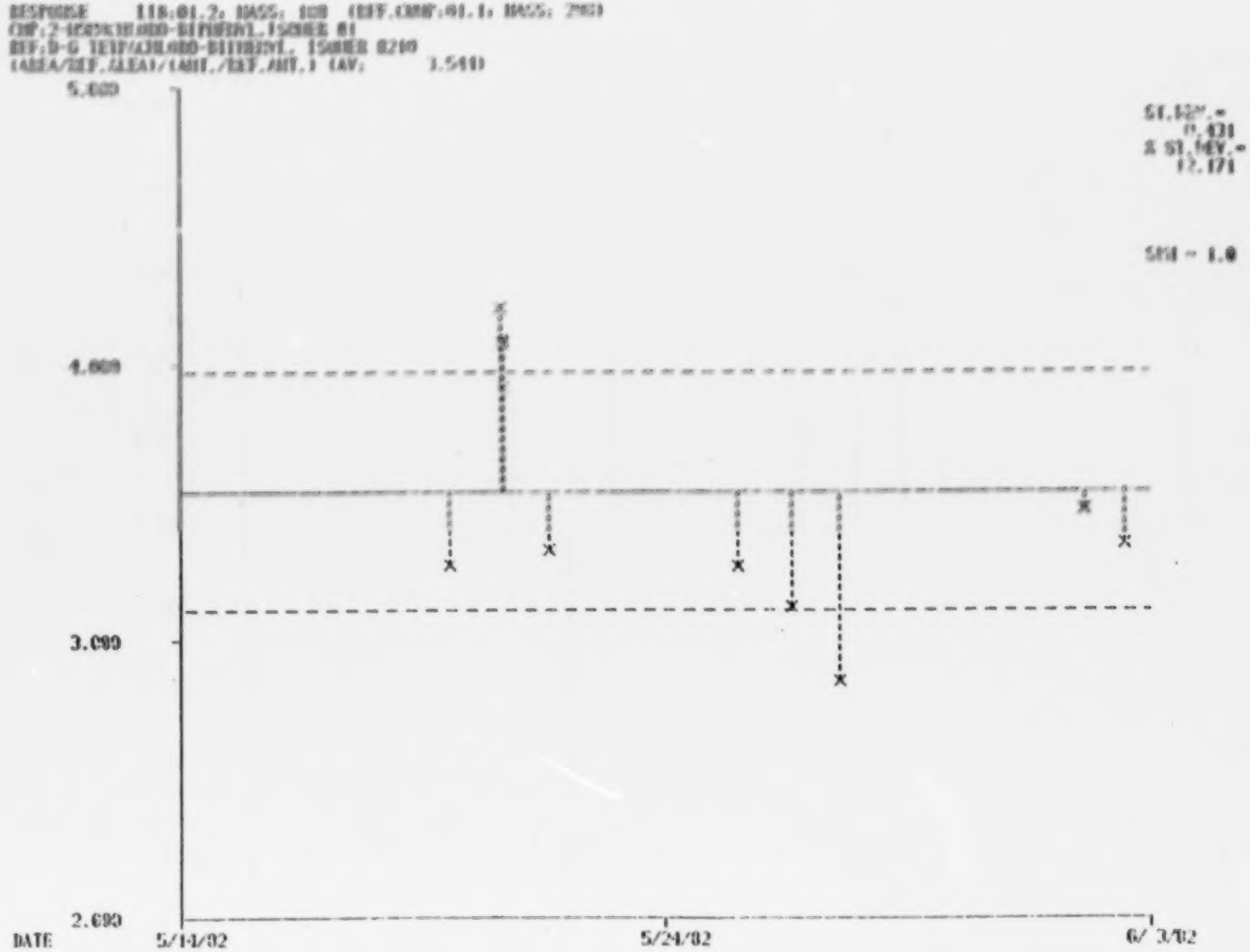

Figure A-14. Relative response factor for 2-monochlorobiphenyl in Solution No. 1 calculated versus 3,3',4,4'-tetrachlorobiphenyl-d$_6$ on a day-to-day basis.

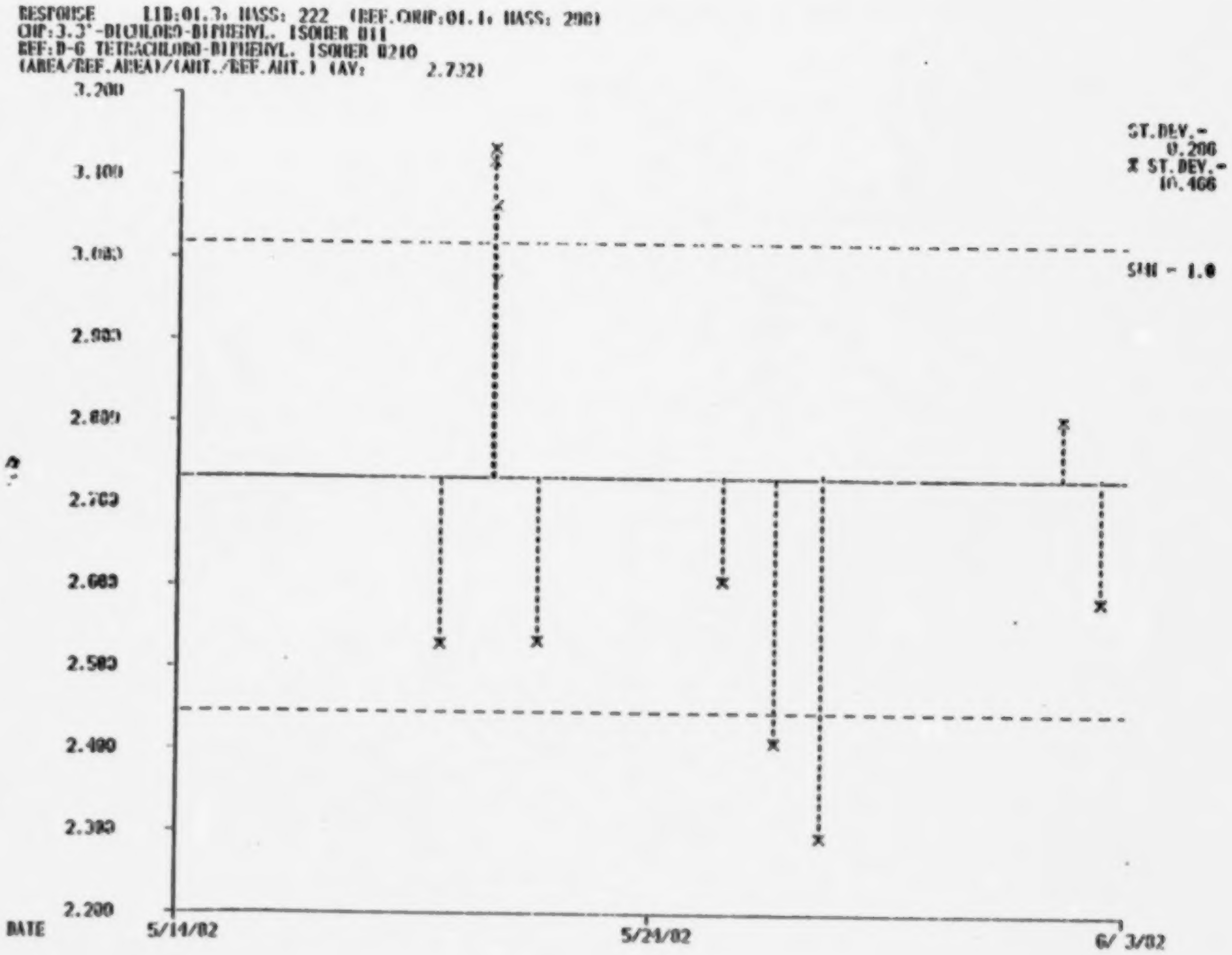

Figure A-15. Relative response factor for 3,3'-dichlorobiphenyl in Solution No. 1 calculated versus 3,3',4,4'-tetrachlorobiphenyl-d_6 on a day-to-day basis.

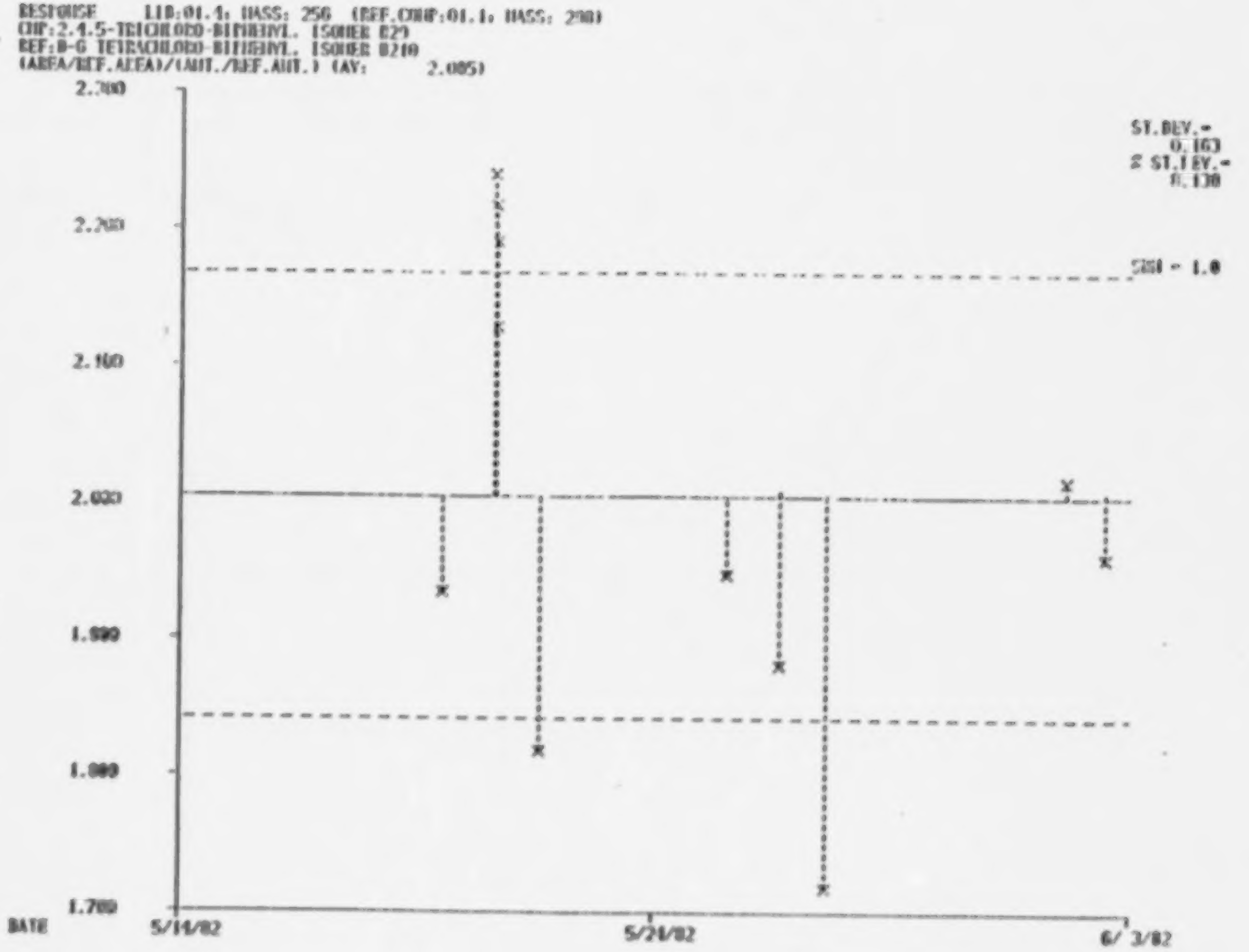

Figure A-16. Relative response factor for 2,4,5-trichlorobiphenyl in Solution No. 1 calculated versus 3,3',4,4'-tetrachlorobiphenyl-d_6 on a day-to-day basis.

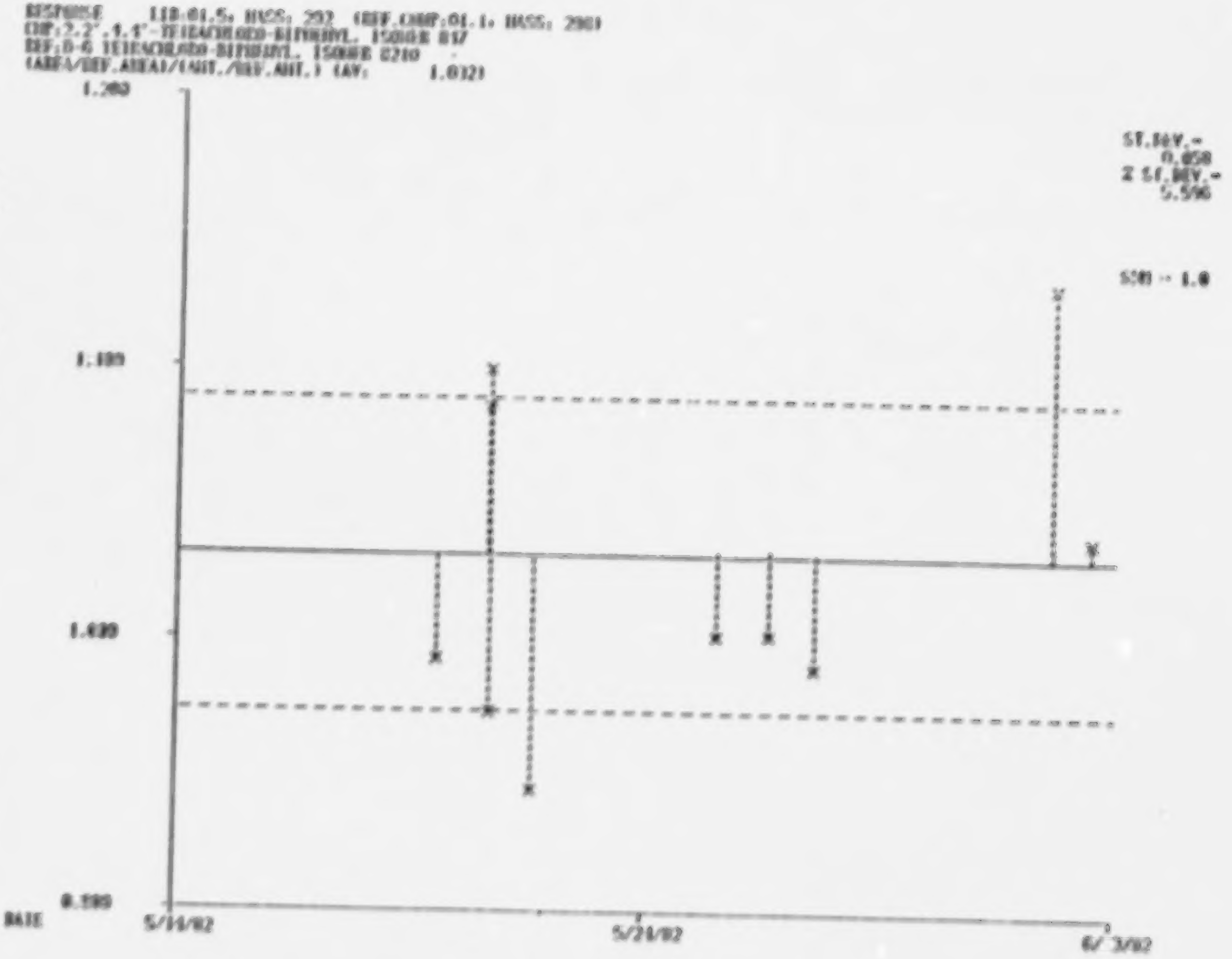

Figure A-17. Relative response factor for 2,2',4,4'-tetrachlorobiphenyl in Solution No. 1 calculated versus 3,3',4,4'-tetrachlorobiphenyl-d_6 on a day-to-day basis.

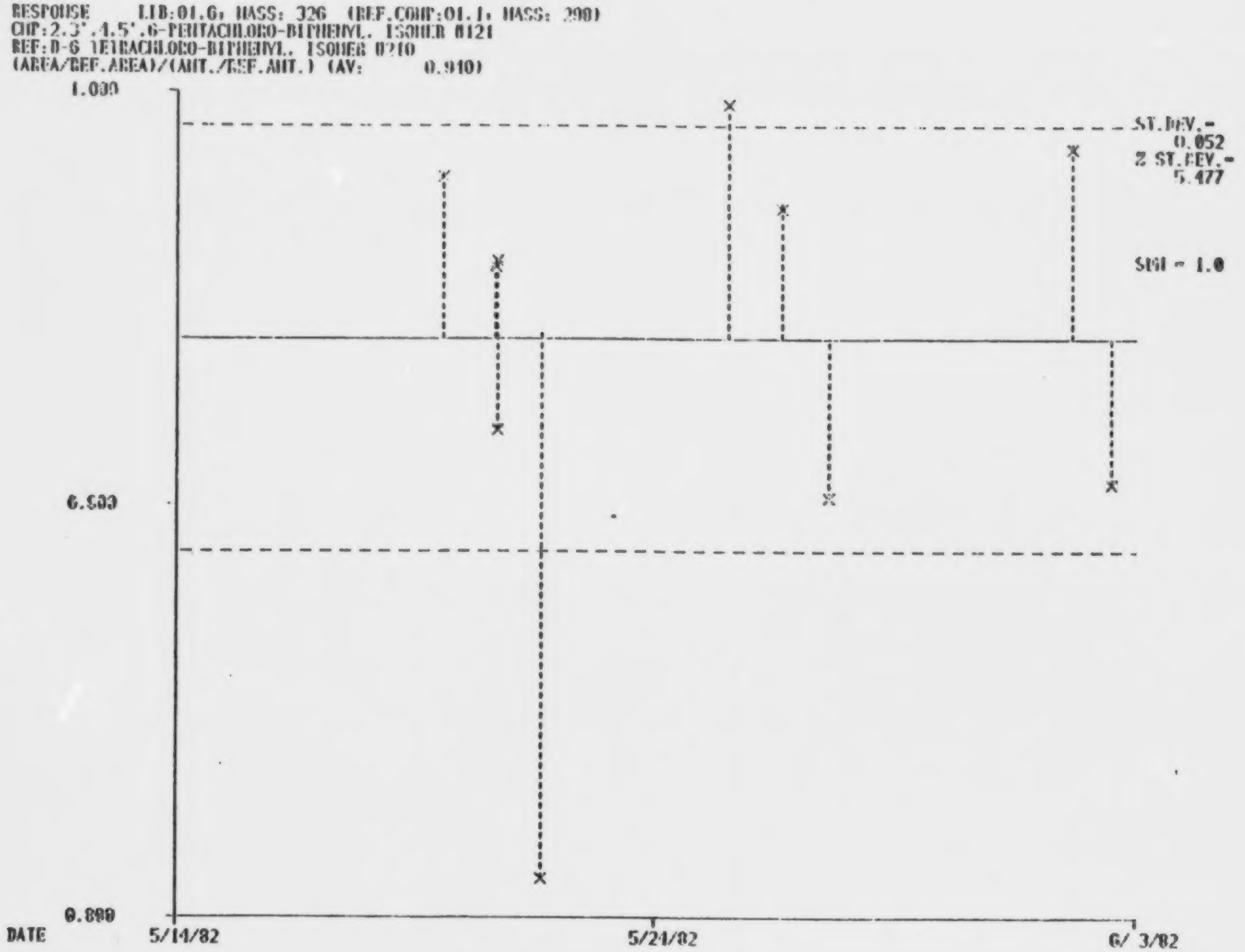

Figure A-18. Relative response factor for 2,3',4,5',6-pentachlorobiphenyl in Solution No. 1 calculated versus 3,3',4,4'-tetrachlorobiphenyl-d_6 on a day-to-day basis.

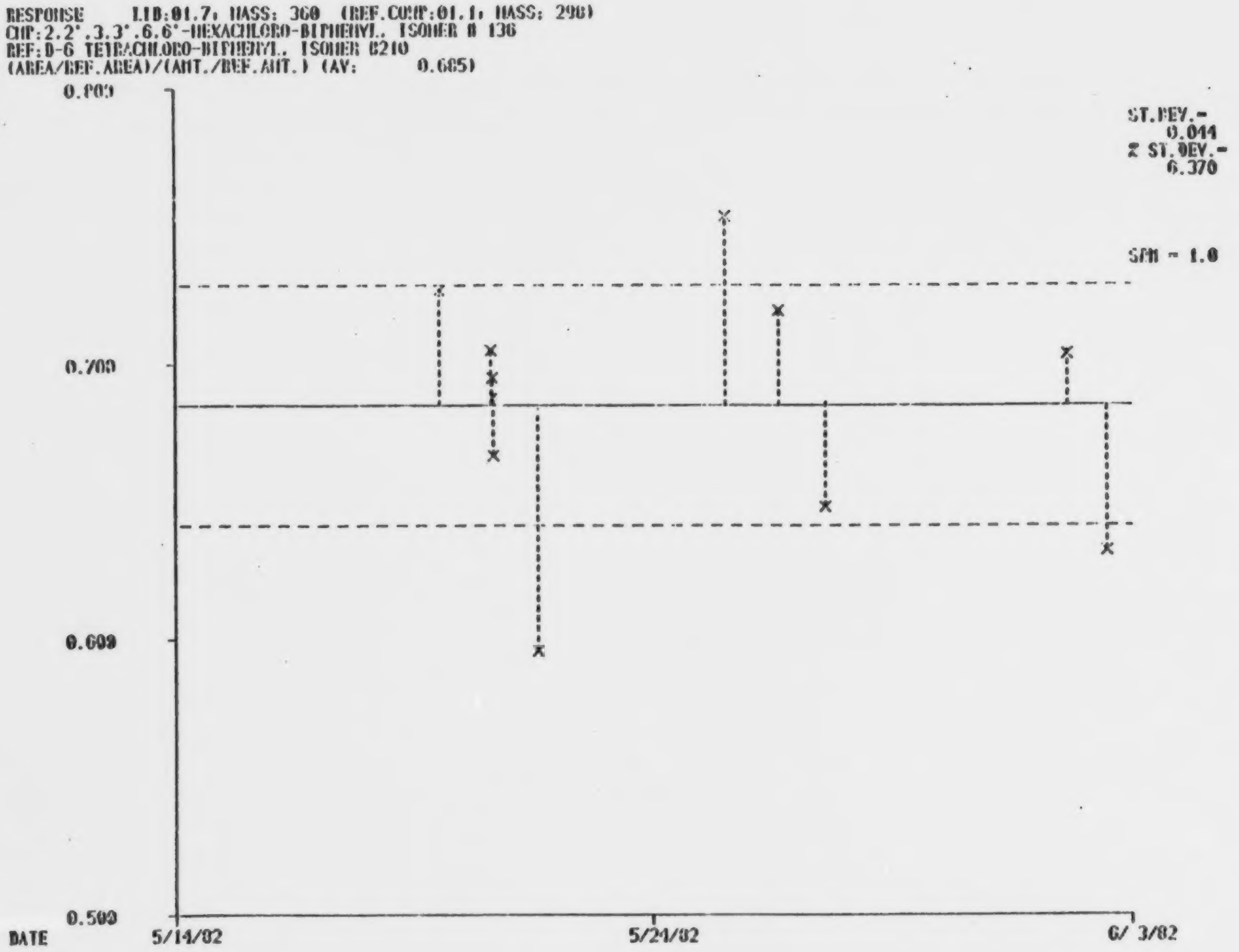

Figure A-19. Relative response factor for 2,2',3,',6,6'-hexachlorobiphenyl in Solution No. 1 calculated versus 3,3',4,4'-tetrachlorobiphenyl-d_6 on a day-to-day basis.

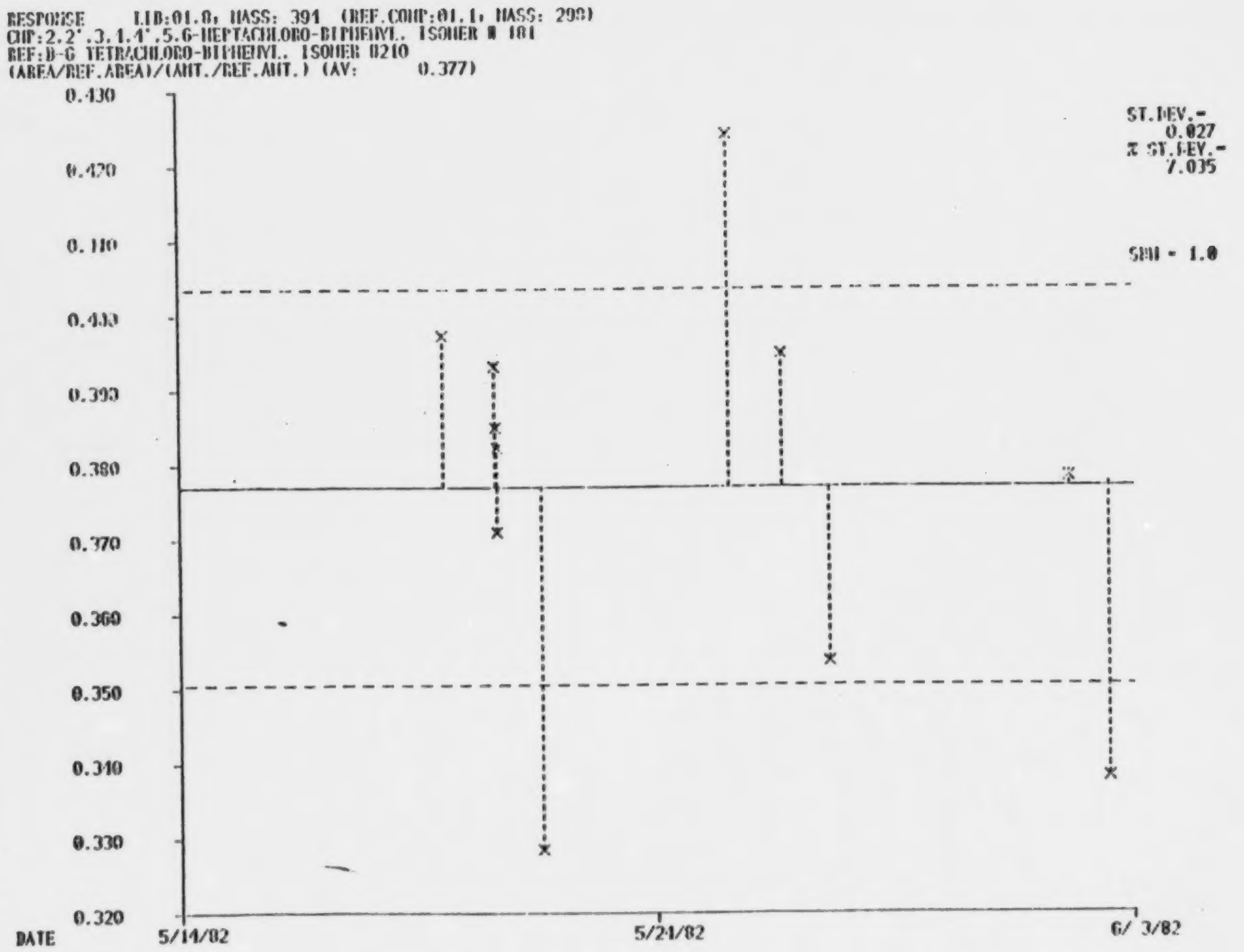

Figure A-20. Relative response factor for 2,2',3,4,4',5,6-heptachlorobiphenyl in Solution No. 1 calculated versus 3,3',4,4'-tetrachlorobiphenyl-d_6 on a day-to-day basis.

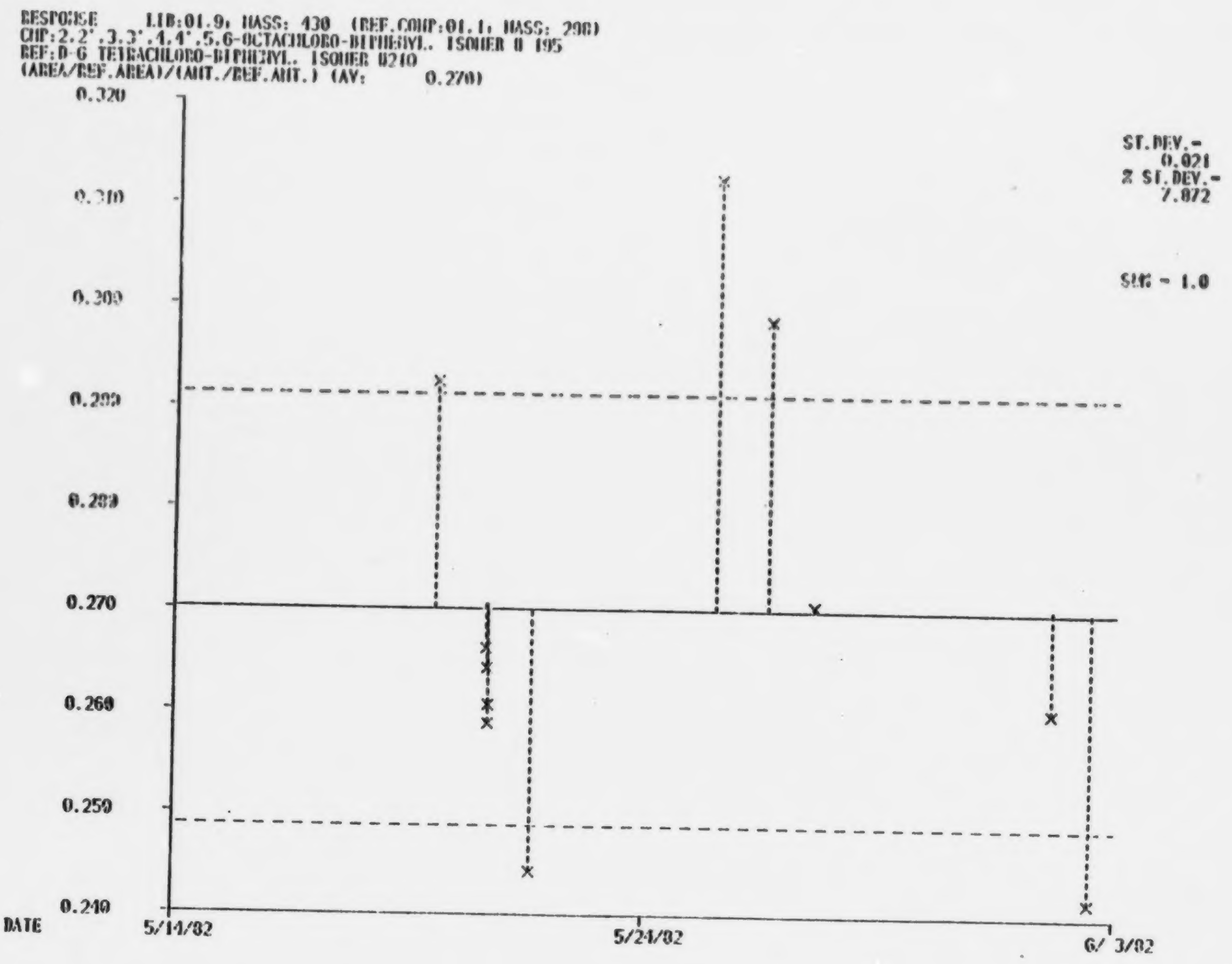

Figure A-21. Relative response factor for 2,2',3,3',4,4',5,6-octachlorobiphenyl in Solution No. 1 calculated versus 3,3',4,4'-tetrachlorobiphenyl-d_6 on a day-to-day basis.

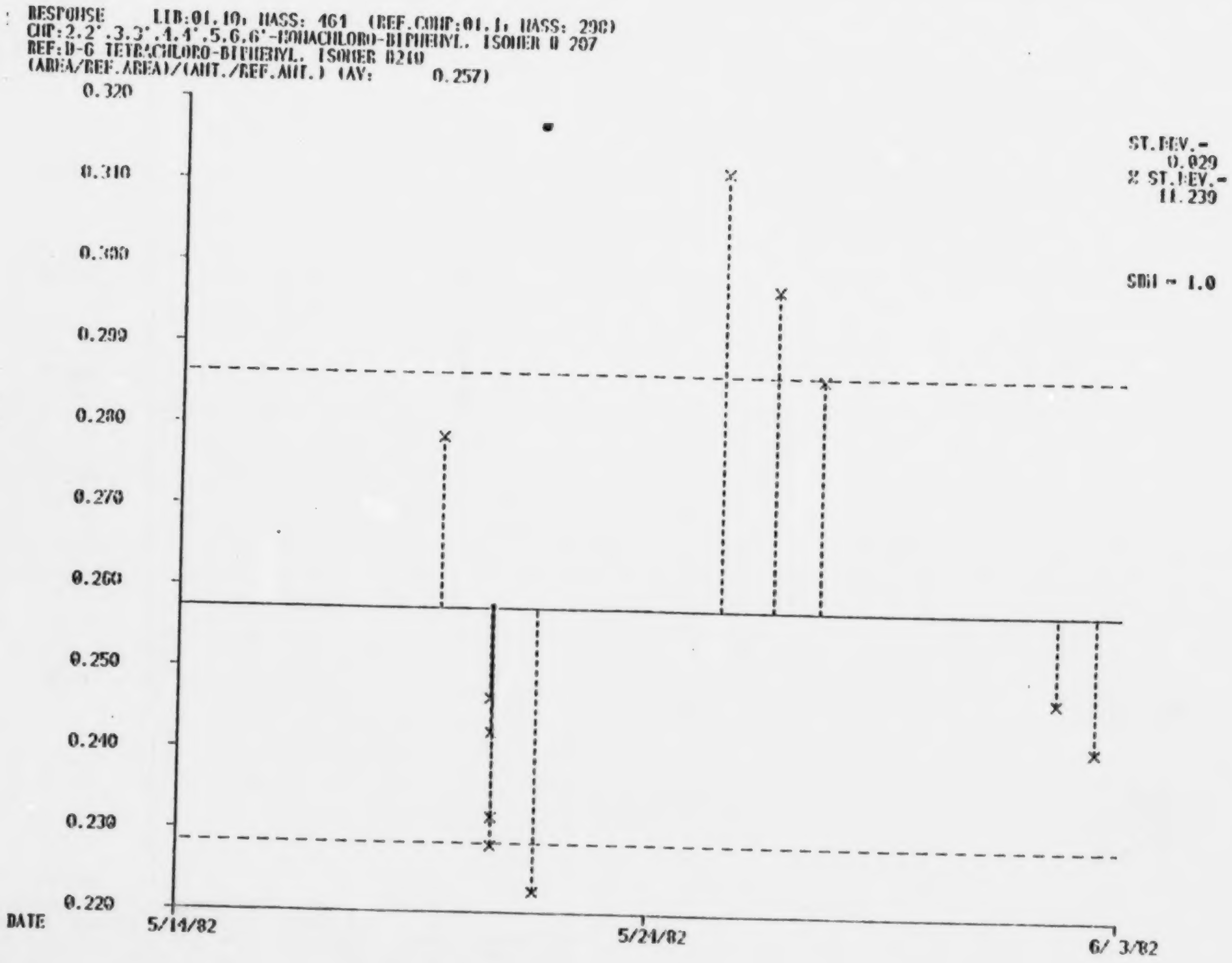

Figure A-22. Relative response factor for 2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl in Solution No. 1 calculated versus 3,3',4,4'-tetrachlorobiphenyl-d_6 on a day-to-day basis.

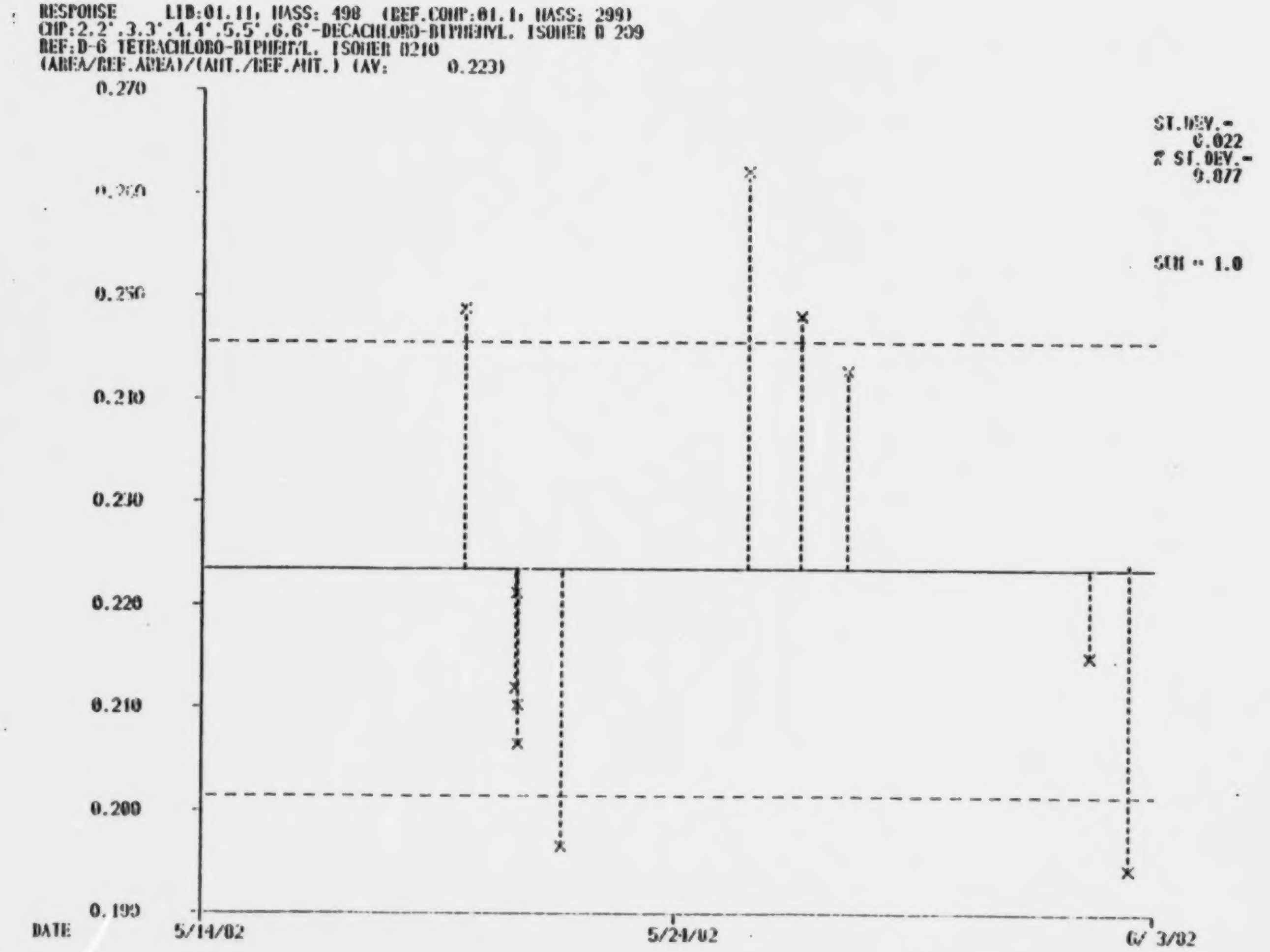

Figure A-23. Relative response factor for 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl in Solution No. 1 calculated versus 3,3',4,4'-tetrachlorobiphenyl-d_6 on a day-to-day basis.

APPENDIX B

ANALYTICAL METHOD: THE ANALYSIS OF BY-PRODUCT CHLORINATED BIPHENYLS IN COMMERCIAL PRODUCTS AND PRODUCT WASTES

THE ANALYSIS OF BY-PRODUCT CHLORINATED BIPHENYLS IN COMMERCIAL PRODUCTS AND PRODUCT WASTES

1.0 Scope and Application

1.1 This is a gas chromatographic/electron impact mass spectrometric (GC/EIMS) method applicable to the determination of chlorinated biphenyls (PCBs) in commercial products and product wastes. The PCBs present may originate either as synthetic by-products or as contaminants derived from commercial PCB products (e.g., Aroclors). The PCBs may be present as single isomers or complex mixtures and may include all 209 congeners from monochlorobiphenyl through decachlorobiphenyl listed in Table 1.

1.2 The detection and quantitation limits are dependent upon the complexity of the sample matrix and the ability of the analyst to remove interferents and properly maintain the analytical system. The method accuracy and precision will be determined in future studies.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography/mass spectrometry (GC/MS) and in the interpretation of gas chromatograms and mass spectra. Prior to sample analysis, each analyst must demonstrate the ability to generate acceptable results with this method by following the procedures described in Section 14.2.

1.4 The validity of the results depends on equivalent recovery of the analyte and ^{13}C PCBs. If the ^{13}C PCBs are not thoroughly incorporated in the matrix, the method is not applicable.

1.5 During the development and testing of this method, certain analytical parameters and equipment designs were found to affect the validity of the analytical results. Proper use of the method requires that such parameters or designs must be used as specified. These items are identified in the text by the word "must." Anyone wishing to deviate from the method in areas so identified must demonstrate that the deviation does not affect the validity of the data. Alternative test procedure approval must be obtained from the Agency. An experienced analyst may make modifications to parameters or equipment identified by the term "recommended." Each time such modifications are made to the method, the analyst must repeat the procedure in Section 14.2. In this case, formal approval is not required, but the documented data from Section 14.2 must be on file as part of the overall quality assurance program.

TABLE 1. NUMBERING OF PCB CONGENERS[a]

No.	Structure
	Monochlorobiphenyls
1	2
2	3
3	4
	Dichlorobiphenyls
4	2,2'
5	2,3
6	2,3'
7	2,4
8	2,4'
9	2,5
10	2,6
11	3,3'
12	3,4
13	3,4'
14	3,5
15	4,4'
	Trichlorobiphenyls
16	2,2',3
17	2,2',4
18	2,2',5
19	2,2',6
20	2,3,3'
21	2,3,4
22	2,3,4'
23	2,3,5
24	2,3,6
25	2,3',4
26	2,3',5
27	2,3',6
28	2,4,4'
29	2,4,5
30	2,4,6
31	2,4',5
32	2,4',6
33	2',3,4
34	2',3,5
35	3,3',4
36	3,3',5
37	3,4,4'
38	3,4,5
39	3,4',5
	Tetrachlorobiphenyls
40	2,2',3,3'
41	2,2',3,4
42	2,2',3,4'
43	2,2',3,5
44	2,2',3,5'
45	2,2',3,6
46	2,2',3,6'
47	2,2',4,4'
48	2,2',4,5
49	2,2',4,5'
50	2,2',4,6
51	2,2',4,6'
	Tetrachlorobiphenyls
52	2,2',5,5'
53	2,2',5,6'
54	2,2',6,6'
55	2,3,3',4
56	2,3,3',4'
57	2,3,3',5
58	2,3,3',5'
59	2,3,3',6
60	2,3,4,4'
61	2,3,4,5
62	2,3,4,6
63	2,3,4',5
64	2,3,4',6
65	2,3,5,6
66	2,3',4,4'
67	2,3',4,5
68	2,3',4,5'
69	2,3',4,6
70	2,3',4',5
71	2,3',4',6
72	2,3',5,5'
73	2,3',5',6
74	2,4,4',5
75	2,4,4',6
76	2',3,4,5
77	3,3',4,4'
78	3,3',4,5
79	3,3',4,5'
80	3,3',5,5'
81	3,4,4',5
	Pentachlorobiphenyls
82	2,2',3,3',4
83	2,2',3,3',5
84	2,2',3,3',6
85	2,2',3,4,4'
86	2,2',3,4,5
87	2,2',3,4,5'
88	2,2',3,4,6
89	2,2',3,4,6'
90	2,2',3,4',5
91	2,2',3,4',6
92	2,2',3,5,5'
93	2,2',3,5,6
94	2,2',3,5,6'
95	2,2',3,5',6
96	2,2',3,6,6'
97	2,2',3',4,5
98	2,2',3',4,6
99	2,2',4,4',5
100	2,2',4,4',6
101	2,2',4,5,5'
102	2,2',4,5,6'
103	2,2',4,5',6
104	2,2',4,6,6'
	Pentachlorobiphenyls
105	2,3,3',4,4'
106	2,3,3',4,5
107	2,3,3',4',5
108	2,3,3',4,5'
109	2,3,3',4,6
110	2,3,3',4',6
111	2,3,3',5,5'
112	2,3,3',5,6
113	2,3,3',5',6
114	2,3,4,4',5
115	2,3,4,4',6
116	2,3,4,5,6
117	2,3,4',5,6
118	2,3',4,4',5
119	2,3',4,4',6
120	2,3',4,5,5'
121	2,3',4,5',6
122	2',3,3',4,5
123	2',3,4,4',5
124	2',3,4,5,5'
125	2',3,4,5,6'
126	3,3',4,4',5
127	3,3',4,5,5'
	Hexachlorobiphenyls
128	2,2',3,3',4,4'
129	2,2',3,3',4,5
130	2,2',3,3',4,5'
131	2,2',3,3',4,6
132	2,2',3,3',4,6'
133	2,2',3,3',5,5'
134	2,2',3,3',5,6
135	2,2',3,3',5,6'
136	2,2',3,3',6,6'
137	2,2',3,4,4',5
138	2,2',3,4,4',5'
139	2,2',3,4,4',6
140	2,2',3,4,4',6'
141	2,2',3,4,5,5'
142	2,2',3,4,5,6
143	2,2',3,4,5,6'
144	2,2',3,4,5',6
145	2,2',3,4,6,6'
146	2,2',3,4',5,5'
147	2,2',3,4',5,6
148	2,2',3,4',5,6'
149	2,2',3,4',5',6
150	2,2',3,4',6,6'
151	2,2',3,5,5',6
152	2,2',3,5,6,6'
153	2,2',4,4',5,5'
154	2,2',4,4',5,6'
155	2,2',4,4',6,6'
156	2,3,3',4,4',5
157	2,3,3',4,4',5'
158	2,3,3',4,4',6
159	2,3,3',4,5,5'
160	2,3,3',4,5,6
	Hexachlorobiphenyls
161	2,3,3',4,5',6
162	2,3,3',4',5,5'
163	2,3,3',4',5,6
164	2,3,3',4',5',6
165	2,3,3',5,5',6
166	2,3,4,4',5,6
167	2,3',4,4',5,5'
168	2,3',4,4',5',6
169	3,3',4,4',5,5'
	Heptachlorobiphenyls
170	2,2',3,3',4,4',5
171	2,2',3,3',4,4',6
172	2,2',3,3',4,5,5'
173	2,2',3,3',4,5,6
174	2,2',3,3',4,5,6'
175	2,2',3,3',4,5',6
176	2,2',3,3',4,6,6'
177	2,2',3,3',4',5,6
178	2,2',3,3',5,5',6
179	2,2',3,3',5,6,6'
180	2,2',3,4,4',5,5'
181	2,2',3,4,4',5,6
182	2,2',3,4,4',5,6'
183	2,2',3,4,4',5',6
184	2,2',3,4,4',6,6'
185	2,2',3,4,5,5',6
186	2,2',3,4,5,6,6'
187	2,2',3,4',5,5',6
188	2,2',3,4',5,6,6'
189	2,3,3',4,4',5,5'
190	2,3,3',4,4',5,6
191	2,3,3',4,4',5',6
192	2,3,3',4,5,5',6
193	2,3,3',4',5,5',6
	Octachlorobiphenyls
194	2,2',3,3',4,4',5,5'
195	2,2',3,3',4,4',5,6
196	2,2',3,3',4,4',5,6'
197	2,2',3,3',4,4',6,6'
198	2,2',3,3',4,5,5',6
199	2,2',3,3',4,5,6,6'
200	2,2',3,3',4,5',6,6'
201	2,2',3,3',4,5,5',6'
202	2,2',3,3',5,5',6,6'
203	2,2',3,4,4',5,5',6
204	2,2',3,4,4',5,6,6'
205	2,3,3',4,4',5,5',6
	Nonachlorobiphenyls
206	2,2',3,3',4,4',5,5',6
207	2,2',3,3',4,4',5,6,6'
208	2,2',3,3',4,5,5',6,6'
	Decachlorobiphenyl
209	2,2',3,3'4,4',5,5',6,6'

[a] Adopted from Ballschmiter, K. and Zell, M., Fresenius Z. Anal. Chem., 302, 20-31 (1980).

2.0 Summary

2.1 The process or product must be sampled such that the specimen collected for analysis is representative of the whole. Statistically designed selection of the sampling position, time, or discrete product units should be employed. The sample must be preserved to prevent PCB loss prior to analysis. Customary inventory storage may be adequate for products. For intermediates, process samples, and other non-product specimens, storage at 4°C with optional preservation at low pH is recommended.

2.2 The sample is mechanically homogenized and subsampled if necessary. The sample is then spiked with four ^{13}C PCB surrogates and the surrogates incorporated by further mechanical agitation.

2.3 The surrogate-spiked sample is extracted and cleaned up at the discretion of the analyst. Simple dilution or direct injection is permissible. Possible extraction techniques include liquid-liquid partition, thermal desorption, and sorption onto resin columns followed by solvent desorption. Cleanup techniques may include liquid-liquid partition, sulfuric acid cleanup, saponification, adsorption chromatography, gel permeation chromatography, or a combination of cleanup techniques. The sample is diluted or concentrated to a final known volume for instrumental determination.

2.4 The PCB content of the sample extract is determined by capillary (preferred) or packed column gas chromatography/electron impact mass spectrometry (CGC/EIMS or PGC/EIMS) operated in the selected ion monitoring (SIM), full scan, or limited mass scan (LMS) mode.

2.5 PCBs are identified by comparison of their retention time and mass spectral intensity ratios to those in calibration standards.

2.6 PCBs are quantitated against the response factors for a mixture of 11 PCB congeners, using the response of the ^{13}C surrogate to compensate for losses in workup and determination and instrument variability.

2.7 The PCBs identified by the SIM technique may be confirmed by full scan CGC/EIMS, retention on alternate GC columns, other mass spectrometric techniques, infrared spectrometry, or other techniques, provided that the sensitivity and selectivity of the technique are demonstrated to be comparable or superior to GC/EIMS.

2.8 The analysis time is dependent on the extent of workup employed. The time required for instrumental analysis of a single sample, excluding data reduction and reporting, is about 30 to 45 min.

2.9 Appropriate quality control (QC) procedures are included to assess the performance of the analyst and estimate the quality of the results. These QC procedures include the demonstration of laboratory capability: periodic analyst certification, the use of control charts, and the analysis of blanks, replicates, and standard addition samples. A quality assurance (QA) plan must be developed for each laboratory.

2.10 While several options are available throughout this method, the recommended procedure to be followed is:

2.10.1 The sample is collected according to a scheme which permits extrapolation of the sample data to the whole product or product waste.

2.10.2 The sample is preserved to prevent any loss of PCBs or changes in matrix which may adversely affect recovery.

2.10.3 The sample is mechanically homogenized and subsampled if necessary.

2.10.4 The sample is spiked with four ^{13}C PCB surrogates (4-chlorobiphenyl; 3,3',4,4'-tetrachlorobiphenyl; 2,2',3,3',5,5',6,6'-octachlorobiphenyl; and decachlorobiphenyl).

2.10.5 Normally, the sample is extracted, although dilution may also be used.

2.10.6 The extract is cleaned up and concentrated to an appropriate volume.

2.10.7 An aliquot of the extract is analyzed by CGC/EIMS operated in the SIM mode. On-column injections onto a 15-m DB-5 capillary column, programmed (for toluene solutions) from 110° to 325°C at 10°/min after a 2-min hold is used. Helium at 45-cm/sec linear velocity is used as the carrier gas.

2.10.8 PCBs are identified by retention time and mass spectral intensities.

2.10.9 PCBs are quantitated against the response factors for a mixture of 11 PCB congeners.

2.10.10 The total PCBs are obtained by summing the amounts for each homolog found, and the concentration is reported as micrograms per gram.

3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware, leading to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences by the analysis of laboratory reagent blanks as described in Section 14.4.

3.1.1 Glassware must be scrupulously cleaned. All glassware is cleaned as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water and rinses with tap water and reagent water. The glassware should then be drained dry and heated in a muffle furnace at 400°C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After it is dry and cool, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. It is stored inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required. All solvent lots must be checked for purity prior to use.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the sources of samples.

4.0 Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

4.2 Polychlorinated biphenyls have been tentatively classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood. Personnel must wear protective equipment, including gloves and safety glasses.

Congeners highly substituted at the meta and para positions and unsubstituted at the ortho positions are reported to be the most toxic. Extreme caution should be taken when handling these compounds neat or in concentrated solutions. This class includes 3,3',4,4'-tetrachlorobiphenyl (both natural abundance and isotopically labeled).

4.3 Diethyl ether should be monitored regularly to determine the peroxide content. Under no circumstances should diethyl ether be used with a peroxide content in excess of 50 ppm, as an explosion could result. Peroxide test strips manufactured by EM Laboratories (available from Scientific Products Company, Cat. No. P1126-8 and other suppliers) are recommended for this test. Procedures for removal of peroxides from diethyl ether are included in the instructions supplied with the peroxide test kit.

4.4 Waste disposal must be in accordance with RCRA and applicable state rules.

5.0 Apparatus and Materials

5.1 Sampling containers - Amber glass bottles, 1-liter or other appropriate volume, fitted with screw caps lined with Teflon. Cleaned foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, samples should be protected from light using foil or a light-tight outer container. The bottle must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.2 Glassware - All specifications are suggestions only. Catalog numbers are included for illustration only.

5.2.1 Volumetric flasks - Assorted sizes.

5.2.2 Pipets - Assorted sizes, Mohr delivery.

5.2.3 Micro syringes - 10.0 µl for packed column GC analysis, 1.0 µl for on-column GC analysis.

5.2.4 Chromatographic column - Chromaflex, 400 mm long x 19 mm ID (Kontes K-420540-9011 or equivalent).

5.2.5 Gel permeation chromatograph - GPC Autoprep 1002 (Analytical Bio Chemistry Laboratories, Inc.) or equivalent.

5.2.6 Kuderna-Danish Evaporative Concentrator Apparatus

5.2.6.1 Concentrator tube - 10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper size (Ŧ19/22 joint) is used to prevent evaporation of solvent.

5.2.6.2 Evaporative flask - 500 ml (Kontes K-57001-0500 or equivalent). Attached to concentrator tube with springs (Kontes K-662750-0012 or equivalent).

5.2.6.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

5.3 Balance - Analytical, capable of accurately weighing 0.0001 g.

5.4 Gas chromatography/mass spectrometer system.

5.4.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using capillary columns or packed columns. Other capillary injection techniques (split, splitless, "Grob," etc.) may be used provided the performance specifications stated in Section 7.1 are met.

5.4.2 Capillary GC column - A 12-20 m long x 0.25 mm ID fused silica column with a 0.25 µm thick DB-5 bonded silicone liquid phase (J&W Scientific) is recommended. Alternate liquid phases may include OV-101, SP-2100, Apiezon L, Dexsil 300, or other liquid phases which meet the performance specifications stated in Section 7.1.

5.4.3 Packed GC column - A 180 cm x 0.2 cm ID glass column packed with 3% SP-2250 on 100/120 mesh Supelcoport or equivalent is recommended. Other liquid phases which meet the performance specifications stated in Section 7.1 may be substituted.

5.4.4 Mass spectrometer - Must be capable of scanning from 150 to 550 daltons every 1.5 sec or less, collecting at least five spectra per chromatographic peak, utilizing a 70-eV (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of decafluorotriphenyl phosphine [DFTPP, bis(perfluorophenyl)phenyl phosphine] is injected through the GC inlet. Any GC-to-MS interface that gives acceptable calibration points at 10 ng per injection for each PCB isomer in the calibration standard and achieves all acceptable performance criteria (Section 10) may be used. Direct coupling of the fused silica column to the MS is recommended. Alternatively, GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.4.5 A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The data system must have the capability of integrating the abundances of the selected ions between specified limits and relating integrated abundances to concentrations using the calibration procedures described in this method. The computer must have software that allows

TABLE 2. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion abundance criteria
197	Less than 1% of mass 198
198	100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present, but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number to yield an extracted ion current profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

6.0 Reagents

6.1 Solvents - All solvents must be pesticide residue analysis grade. New lots should be checked for purity by concentrating an aliquot by at least as much as is used in the procedure.

6.2 Calibration standard congeners - Standards of the PCB congeners listed in Table 3 are available from Ultra Scientific, Hope, Rhode Island; or Analabs, North Haven, Connecticut.

6.3 Calibration standard stock solutions - Primary dilutions of each of the individual PCBs listed in Table 3 are prepared by weighing approximately 1-10 mg of material within 1% precision. The PCB is then dissolved and diluted to 1.0 ml with hexane. The concentration is calculated in mg/ml. The primary dilutions are stored at 4°C in screw-cap vials with Teflon cap liners. The meniscus is marked on the vial wall to monitor solvent evaporation. Primary dilutions are stable indefinitely if the seals are maintained. The validity of primary and secondary dilutions must be monitored on a quarterly basis by analyzing four quality control check samples (see Section 14.2).

6.4 Working calibration standards - Working calibration standards are prepared that are similar in PCB composition and concentration to the samples by mixing and diluting the individual standard stock solutions. Example calibration solutions are shown in Table 3. The mixture is diluted to volume with pesticide residue analysis quality hexane. The concentration is calculated in ng/ml as the individual PCBs. Dilutions are stored at 4°C in narrow-mouth, screw-cap vials with Teflon cap liners. The meniscus is marked on the vial wall to monitor solvent evaporation. These secondary dilutions can be stored indefinitely if the seals are maintained. These solutions are designated "CSxxx," where the xxx is used to encode the nominal concentration in ng/ml.

6.5 Alternatively, certified stock solutions similar to those listed in Table 3 may be available from a supplier, in lieu of the procedure described in Section 6.4.

6.6 DFTPP standard - A 50-ng/µl solution of DFTPP is prepared in acetone or another appropriate solvent.

6.7 Surrogate standard stock solution - The four ^{13}C-labeled PCBs listed in Table 4 may be available from a supplier as a certified solution. This solution may be used as received or diluted further. These solutions are designated "SSxxx," where the xxx is used to encode the nominal concentration in µg/ml.

TABLE 3. CONCENTRATIONS OF CONGENERS IN PCB CALIBRATION STANDARDS (ng/ml)[a]

Homolog	Congener no.	CS1000	CS100	CS050	CS010
1	1	1,040	104	52	10
1	3	1,000	100	50	10
2	7	1,040	104	52	10
3	30	1,040	104	52	10
4	50	1,520	152	76	15
5	97	1,740	174	87	17
6	143	1,920	192	96	19
7	183	2,600	260	130	26
8	202	4,640	464	232	46
9	207	5,060	506	253	51
10	209	4,240	424	212	42
4	210 (IS)	255	255	255	255
1	211 (RS)	104	104	104	104
4	212 (RS)	257	257	257	257
8	213 (RS)	407	407	407	407
10	214 (RS)	502	502	502	502

---

[a] Concentrations given as examples only.

TABLE 4. COMPOSITION OF SURROGATE SPIKING SOLUTION (SS100) CONTAINING ^{13}C-LABELED PCBs[a]

Congener no.	Compound	Concentration (µg/ml)
211	$(1',2',3',4',5',6'-^{13}C_6)$4-chlorobiphenyl	104
212	$(^{13}C_{12})$3,3',4,4'-tetrachlorobiphenyl	257
213	$(^{13}C_{12})$2,2',3,3',5,5',6,6'-octachlorobiphenyl	395
214	$(^{13}C_{12})$decachlorobiphenyl	502

[a] Concentrations given as examples only.

6.8 Internal standard solution - A solution of d_6-3,3',4,4'-tetrachlorobiphenyl is prepared at a nominal concentration of 1-10 mg/ml in hexane. The solution is further diluted to give a working standard.

6.9 Solution stability - The calibration standard, surrogate, and DFTPP solutions should be checked frequently for stability. These solutions should be replaced after 6 months, or sooner if comparison with quality control check samples indicates compound degradation or concentration change.

6.10 Quality control check samples will be supplied by the Agency.

7.0 Calibration

7.1 The gas chromatograph must meet the minimum operating parameters shown in Tables 5 and 6, daily. If all criteria are not met, the analyst must adjust conditions and repeat the test until all criteria are met.

7.2 The mass spectrometer must meet the minimum operating parameters shown in Tables 2, 7, and 8, daily. If all criteria are not met, the analyst must retune the spectrometer and repeat the test until all conditions are met.

7.3 The PCB response factors (RF_p) must be determined using Equation 7-1 for the analyte homologs.

$$RF_p = \frac{A_p \times M_{is}}{A_{is} \times M_p} \qquad \text{Eq. 7-1}$$

where RF_p = response factor of a given PCB congener

A_p = area of the characteristic ion for the PCB congener peak

M_p = mass of PCB congener injected (nanograms)

A_{is} = area of the characteristic ion for the internal standard peak

M_{is} = mass of internal standard injected (nanograms)

Using the same conditions as for RF_p, the surrogate response factors (RF_s) must be determined using Equation 7-2.

$$RF_s = \frac{A_s \times M_{is}}{A_{is} \times M_s} \qquad \text{Eq. 7-2}$$

where A_s = area of the characteristic ion for the surrogate peak

M_s = mass of surrogate injected (nanograms)

Other terms are the same as defined in Equation 7-1.

TABLE 5. OPERATING PARAMETERS FOR CAPILLARY COLUMN GAS CHROMATOGRAPHIC SYSTEM

Parameter	Recommended	Tolerance
Gas chromatograph	Finnigan 9610	Other[a]
Column	15 m x 0.255 mm ID Fused silica	Other
Liquid phase	DB-5 (J&W)	Other nonpolar or semipolar
Liquid phase thickness	0.25 µm	< 1 µm
Carrier gas	Helium	Hydrogen
Carrier gas velocity	45 cm/sec[b]	Optimum performance
Injector	On-column (J&W)[c]	Other
Injector temperature	Optimum performance[c]	Optimum performance
Injection volume	1.0 µl[c]	Other
Initial column temperature	70°C (2 min)[d]	Other
Column temperature program	70°-325°C at 10°C/min[e]	Other
Separator	None[f]	Glass jet or other
Transfer line temperature	280°C	Optimum[g]
Tailing factor[h]	0.7-1.5	0.4-3
Peak width[i]	7-10 sec	< 15 sec

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a Substitutions permitted with any common apparatus or technique provided performance criteria are met.

b Measured by injection of air or methane at 270°C oven temperature.

c For on-column injection, manufacturer's instructions should be followed regarding injection technique.

d With on-column injection, initial temperature equals boiling point of the solvent; in this instance, hexane.

e $C_{12}Cl_{10}$ elutes at 270°C. Programming above this temperature ensures a clean column and lower background on subsequent runs.

f Fused silica columns may be routed directly into the ion source to prevent separator discrimination and losses.

g High enough to elute all PCBs, but not high enough to degrade the column if routed through the transfer line.

h Tailing factor is width of front half of peak at 10% height divided by width of back half of peak at 10% height for single PCB congeners in solution CSxxx.

i Peak width at 10% height for a single PCB congener is CSxxx.

TABLE 6. OPERATING PARAMETERS FOR PACKED COLUMN GAS CHROMATOGRAPHY SYSTEM

Parameter	Recommended	Tolerance
Gas chromatograph	Finnigan 9610	Other[a]
Column	180 cm x 0.2 cm ID glass	Other
Column packing	3% SP-2250 on 100/120 mesh Supelcoport	Other nonpolar or semipolar
Carrier gas	Helium	Hydrogen
Carrier gas flow rate	30 ml/min	Optimum performance
Injector	On-column	Other
Injector temperature	250°C	Optimum[b]
Injection volume	1.0 μl	≦ 5 μl
Initial column temperature	150°C, 4 min	Other
Column temperature program	150°-260°C at 8°/min	Other
Separator	Glass jet	Other
Transfer line temperature	280°C	Optimum[a]
Tailing factor[c]	0.7-1.5	0.4-3
Peak width[d]	10-20 sec	< 30 sec

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[a] Substitutions permitted if performance criteria are met.

[b] High enough to elute all PCBs.

[c] Tailing factor is width of front half of peak at 10% height divided by width of back half of peak at 10% height for single PCB congeners in solution CSxxx.

[d] Peak width at 10% height for a single PCB congener in CSxxx.

TABLE 7. OPERATING PARAMETERS FOR QUADRUPOLE MASS SPECTROMETER SYSTEM

Parameter	Recommended	Tolerance
Mass spectrometer	Finnigan 4023	Other[a]
Data system	Incos 2400	Other
Scan range	95-550	Other
Scan time	1 sec	Other[b]
Resolution	Unit	Optimum performance
Ion source temperature	280°C	200°-300°C
Electron energy[c]	70 eV	Optimum performance
Trap current	0.2 mA	Optimum performance
Multiplier voltage	-1,600 V	Optimum performance
Preamplifier sensitivity	10^{-6} A/V	Set for desired working range

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[a] Substitutions permitted if performance criteria are met.

[b] Greater than five data points over a GC peak is a minimum.

[c] Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no separator is used.

TABLE 8. OPERATING PARAMETERS FOR MAGNETIC SECTOR MASS SPECTROMETER SYSTEM

Parameter	Recommended	Tolerance
Mass spectrometer	Finnigan MAT 311A	Other[a]
Data system	Incos 2400	Other
Scan range	98-550	Other
Scan mode	Exponential	Other
Cycle time	1.2 sec	Other[b]
Resolution	1,000	> 500
Ion source temperature	280°C	250°-300°C
Electron energy[c]	70 eV	70 eV
Emission current	1-2 mA	Optimum
Filament current	Optimum	Optimum
Multiplier	-1,600 V	Optimum

---

[a] Substitutions permitted if performance criteria are met.

[b] Greater than five data points over a GC peak is a minimum.

[c] Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no separator is used.

If specific congeners are known to be present and if standards are available, selected RF values may be employed. For general samples, solutions CSxxx and SSxxx or a mixture (Tables 3 and 4), with a similar level of internal standard (d_6-3,3',4,4'-tetrachlorobiphenyl) added, may be used as the response factor solution. The PCB-surrogate pairs to be used in the RF calculation are listed in Table 9.

Generally, only the primary ions of both the analyte and surrogate are used to determine the RF values. If alternate ions are to be used in the quantitation, the RF must be determined using that characteristic ion.

The RF value must be determined in a manner to assure ±20% accuracy and precision. For instruments with good day-to-day precision, a running mean ($\overline{RF}$) based on seven values determined once each day may be appropriate. Other options include, but are not limited to, triplicate determinations of a single concentration spaced throughout a day or determination of the RF at three different levels to establish a working curve.

If replicate RF values differ by greater than ±10% RSD, the system performance should be monitored closely. If the RSD is greater than ±20%, the data set must be considered invalid and the RF redetermined before further analyses are done.

7.4 If the GC/EIMS system has not been demonstrated to yield a linear response or if the analyte concentrations are more than two orders of magnitude different from those in the RF solution, a calibration curve must be prepared. If the analyte and RF solution concentrations differ by more than one order of magnitude, a calibration curve should be prepared. A calibration curve should be established with triplicate determinations at three or more concentrations bracketing the analyte levels.

7.5 The relative retention time (RRT) windows for the 10 homologs and surrogates must be determined. If all congeners are not available, a mixture of available congeners or an Aroclor mixture (e.g., 1016/1254/1260) may be used to estimate the windows. The windows must be set wider than observed if all isomers are not determined. Typical RRT windows for one column are listed in Table 10. The windows may differ substantially if other GC parameters are used.

8.0 Sample Collection, Handling, and Preservation

8.1 Amber glass sample containers should have Teflon-lined screw caps. With noncorrosive samples, methylene chloride-washed aluminum foil liners may be substituted. The volume and configuration are determined by the amount of sample to be collected and its physical properties. For dry powders, other containers such as heavy-walled polyethylene bags may be appropriate.

TABLE 9. PAIRINGS OF ANALYTE, CALIBRATION, AND SURROGATE COMPOUNDS

Analyte		Calibration standard		Surrogate	
Congener[a] no.	Compound	Congener no.	Compound	Congener no.	Compound
1	2-$C_{12}H_9Cl$	1	2	211	$^{13}C_6$-4
2,3	3- and 4-$C_{12}H_9Cl$	3	4	211	$^{13}C_6$-4
4-15	$C_{12}H_8Cl_2$	7	2,4	211	$^{13}C_6$-4
16-39	$C_{12}H_7Cl_3$	30	2,4,6	212	$^{13}C_{12}$-3,3',4,4'
40-81	$C_{12}H_6Cl_4$	50	2,2',4,6	212	$^{13}C_{12}$-3,3',4,4'
82-127	$C_{12}H_5Cl_5$	97	2,2',3',4,5	212	$^{13}C_{12}$-3,3',4,4'
128-169	$C_{12}H_4Cl_6$	143	2,2',3,4,5,6'	212	$^{13}C_{12}$-3,3',4,4'
170-193	$C_{12}H_3Cl_7$	183	2,2',3',4,4',5',6	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
194-205	$C_{12}H_2Cl_8$	202	2,2',3,3',5,5',6,6'	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
206-208	$C_{12}HCl_9$	207	2,2',3,3',4,4',5,6,6'	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
209	$C_{12}Cl_{10}$	209	$C_{12}Cl_{10}$	214	$^{13}C_{12}Cl_{10}$

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[a] Ballschmiter numbering system, see Table 1.

TABLE 10. RELATIVE RETENTION TIME (RRT) RANGES OF PCB HOMOLOGS VERSUS d_6-3,3',4,4'-TETRACHLOROBIPHENYL

PCB homolog	No. of isomers measured	Observed range of RRTs[a]	Calibration solution		Projected range of RRTs[b]
			Congener no.	Observed RRT[a]	
Monochloro	3	0.40-0.50	1 3	0.43 0.50	0.35-0.55
Dichloro	10	0.52-0.69	7	0.58	0.35-0.80
Trichloro	9	0.62-0.79	30	0.65	0.35-1.10
Tetrachloro	16	0.72-1.01	50	0.75	0.55-1.05
Pentachloro	12	0.82-1.08	97	0.98	0.80-1.10
Hexachloro	13	0.93-1.20	143	1.05	0.90-1.25
Heptachloro	4	1.09-1.30	183	1.15	1.05-1.35
Octachloro	6	1.19-1.36	202	1.19	1.10-1.50
Nonachloro	3	1.31-1.42	207	1.33	1.25-1.50
Decachloro	1	1.44-1.45	209	1.44	1.35-1.50

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[a] The RRTs of the 77 congeners and a mixture of Aroclor 1016/1254/1260 were measured versus 3,3',4,4'-tetrachlorobiphenyl-d_6 (internal standard) using a 15-m J&W DB-5 fused silica column with a temperature program of 110°C for 2 min, then 10°C/min to 325°C, helium carrier at 45 cm/sec, and an on-column injector. A Finnigan 4023 Incos quadrupole mass spectrometer operating with a scan range of 95-550 daltons was used to detect each PCB congener.

[b] The projected relative retention windows account for overlap of eluting homologs and take into consideration differences in operating systems and lack of all possible 209 PCB congeners.

8.2 Sample bottle preparation

8.2.1 All sample containers and caps should be washed in detergent solution, rinsed with tap water, and then with distilled water. The bottles and caps are allowed to drain dry in a contaminant-free area. Then the caps are rinsed with pesticide grade hexane and allowed to air dry.

8.2.2 Sample bottles are heated to 400°C for 15 to 20 min or rinsed with pesticide grade acetone or hexane and allowed to air dry.

8.2.3 The clean bottles are stored inverted or sealed until use.

8.3 Sample collection

8.3.1 The primary consideration in sample collection is that the sample collected be representative of the whole. Therefore, sampling plans or protocols for each individual producer's situation will have to be developed. The recommendations presented here describe general situations. The number of replicates and sampling frequency also must be planned prior to sampling.

8.3.2 Discrete product units - If the product is small enough that one or more discrete units would be used as the analytical sample, a statistically random sampling approach is recommended.

8.3.3 Liquids or free-flowing solids - If possible, the source is mixed thoroughly before collecting the sample. If mixing is impractical, the sample should be collected from a representative area of the source. If the liquid is flowing through an enclosed system, sampling through a valve should be randomly timed.

8.3.4 Solids - Larger bulk solids which must be subsampled to get a reasonably sized analytical sample must be treated on a case-by-case basis. A representative sample should be obtained by designing a sampling location selection scheme such that all parts of the whole have a finite, known probability of inclusion. Based on such a scheme, the PCB content of the sample can be used to extrapolate to the content of the whole.

8.4 Sample preservation - Product samples should be stored as the bulk or packaged product inventory would be stored, or in a cool, dry, dark area. Intermediates, process samples, or other non-product specimens should be stored at 4°C. If there is a possibility of microbial degradation, addition of H_2SO_4 during collection to a $pH < 2$ is recommended. A test strip is used to monitor pH. Storage times in excess of 4 weeks are not recommended.

If residual chlorine is present in the sample, it should be quenched with sodium thiosulfate. EPA Methods 330.4 and 330.5 may be used to measure the residual chlorine.[1] Field test kits are available for this purpose.

9.0 Sample Preparation

Since a wide variety of matrices may be subjected to analysis by this method, the extraction/cleanup procedure cannot be specified. This section describes general guidelines for subsampling, addition of ^{13}C surrogates, dilution, extraction, cleanup, extract concentration, and other sample preparation procedures.

9.1 Sample homogenization and subsampling - The sample is homogenized by shaking, blending, shredding, crushing, or other appropriate mechanical technique. A representative subsample of 100 g or other known mass is then taken. The sample size is dependent upon the anticipated PCB levels and difficulty of the subsequent extraction/cleanup steps.

Note: The precision of the mass determination at this step will be reflected in the overall method precision. Therefore, an analytical balance must be used to assure that the weight is accurate to ±1% or better.

9.2 Surrogate addition - An appropriate volume of surrogate solution SSxxx is pipetted into the sample. The final concentration of the surrogates must be in the working range of the calibration and well above the matrix background. The surrogates are thoroughly incorporated by further mechanical agitation. For nonviscous liquids, shaking for 30 sec should be sufficient. For viscous liquids or free-flowing solids, 10-min tumbling is recommended. In cases where inadequate incorporation may be expected, such as solids, overnight equilibration with agitation is recommended.

Note: The volume measurement of the spiking solution is critical to the overall method precision. The analyst must exercise caution that the volume is known to ±1% or better. Where necessary, calibration of the pipet is recommended.

9.3 Sample preparation (extraction/cleanup) - After addition of the surrogates, the sample is further treated at the discretion of the analyst, provided that the GC/EIMS response of the four surrogates meets the criteria listed in Section 7.0. The literature pertaining to these techniques has been reviewed.[2] Several possible techniques are presented below for guidance only. The applicability of any of these techniques to a specific sample matrix must be determined by the precision and accuracy of the ^{13}C PCB surrogate recoveries, as discussed in Section 14.2.

9.3.1 Extraction

9.3.1.1 Dilution - In some cases, where the PCB concentration is high, a simple volumetric dilution with an appropriate solvent may be sufficient sample preparation.

9.3.1.2 Direct injection - If sample viscosity permits, direct injection with no dilution is permissible.

9.3.1.3 Liquid-liquid extraction - If the matrix is aqueous (or another solvent in which PCBs are only slightly soluble), a liquid-liquid partition may be effective. The solvent, number of extractions, solvent-to-sample ratio, and other parameters are chosen at the analyst's discretion.

9.3.1.4 Sorbent column extraction - PCBs may be isolated from free-flowing liquids onto sorbent columns. The selection of sorbent (XAD, Porapak, carbon-polyurethane foam, etc.) will depend on the nature of the matrix. The available methods have been reviewed.[2]

9.3.1.5 Thermal desorption - If the matrix is nonvolatile, thermal desorption of the PCBs onto a sorbent column, filter, or cold trap may be an effective extraction/cleanup method.

9.3.2 Cleanup - Several tested cleanup techniques are described below. All but the base cleanup (9.3.2.8) were previously validated for PCBs in transformer fluids.[3] Depending upon the complexity of the sample, one or more of the techniques may be required to fractionate the PCBs from interferences. For most cleanups a concentrated (1-5 ml) extract should be used.

9.3.2.1 Acid cleanup

9.3.2.1.1 Place 5 ml of concentrated sulfuric acid into a 40-ml narrow-mouth screw-cap bottle. Add the sample extract. Seal the bottle with a Teflon-lined screw cap and shake for 1 min.

9.3.2.1.2 Allow the phases to separate, transfer the sample (upper phase) with three rinses of 1-2 ml solvent to a clean container and concentrate to an appropriate volume.

9.3.2.1.3 Analyze as described in Section 10.0.

9.3.2.1.4 If the sample is highly contaminated, a second or third acid cleanup may be employed.

9.3.2.2 Florisil column cleanup

9.3.2.2.1 Variations among batches of Florisil (PR grade or equivalent) may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all PCBs must be verified by the analyst. The weight of Florisil can then be adjusted accordingly.

9.3.2.2.2 Place a 20-g charge of Florisil, activated overnight at 130°C, into a Chromaflex column. Settle the Florisil by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the Florisil. Pre-elute the column with 70-80 ml of hexane. Just before the exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

9.3.2.2.3 Add the sample extract to the column.

9.3.2.2.4 Carefully wash down the inner wall of the column with 5 ml of hexane.

9.3.2.2.5 Add 200 ml of 6% ethyl ether/hexane and set the flow to about 5 ml/min.

9.3.2.2.6 Collect 200 ml of eluate in a Kuderna-Danish flask. All the PCBs should be in this fraction. Concentrate to an appropriate volume.

9.3.2.2.7 Analyze the sample as described in Section 10.0.

9.3.2.3 Alumina column cleanup

9.3.2.3.1 Adjust the activity of the alumina (Fisher A450 or equivalent) by heating to 200°C for 2 to 4 hr. When cool, add 3% water (wt:wt) and mix until uniform. Store in a tightly sealed bottle. Allow the deactivated alumina to equilibrate at least 1/2 hr before use. Reactivate weekly.

9.3.2.3.2 Variations between batches of alumina may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of alumina can then be adjusted accordingly.

9.3.2.3.3 Place a 50-g charge of alumina into a Chromaflex column. Settle the alumina by tapping. Add about 1 cm of anhydrous sodium sulfate. Pre-elute the column with 70-80 ml of hexane. Just before exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

9.3.2.3.4 Add the sample extract to the column.

9.3.2.3.5 Carefully wash down the inner wall of the column with 5 ml of hexane.

9.3.2.3.6 Add 295 ml of hexane to the column.

9.3.2.3.7 Discard the first 50 ml.

9.3.2.3.8 Collect 250 ml of the hexane in a Kuderna-Danish flask. All of the PCBs should be in this fraction. Concentrate to an appropriate volume.

9.3.2.3.9 Analyze the sample as described in Section 10.0.

9.3.2.4 Silica gel column cleanup

9.3.2.4.1 Activate silica gel (Davison Grade 950 or equivalent) at 135°C overnight.

9.3.2.4.2 Variations between batches of silica gel may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of silica gel can then be adjusted accordingly.

9.3.2.4.3 Place a 25-g charge of activated silica gel into a Chromaflex column. Settle the silica gel by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the silica gel.

9.3.2.4.4 Pre-elute the column with 70-80 ml of hexane. Discard the eluate. Just before exposing the sodium sulfate layer to air, stop the flow.

9.3.2.4.5 Add the sample extract to the column.

9.3.2.4.6 Wash down the inner wall of the column with 5 ml of hexane.

9.3.2.4.7 Elute the PCBs with 195 ml of 10% diethyl ether in hexane (v:v).

9.3.2.4.8 Collect 200 ml of the eluate in a Kuderna-Danish flask. All of the PCBs should be in this fraction. Concentrate to an appropriate volume.

9.3.2.4.9 Analyze the sample as described in Section 10.0.

9.3.2.5 Gel permeation cleanup

9.3.2.5.1 Set up and calibrate the gel permeation chromatograph with an SX-3 column according to the Autoprep instruction manual. Use 15% methylene chloride in cyclohexane (v:v) as the mobile phase.

9.3.2.5.2 Inject 5.0 ml of the sample extract into the instrument. Collect the fraction containing the PCBs (see Autoprep operator's manual) in a Kuderna-Danish flask equipped with a 10-ml ampul.

9.3.2.5.3 Concentrate the PCB fraction to an appropriate volume.

9.3.2.5.4 Analyze the sample as described in Section 10.0.

9.3.2.6 Acetonitrile partition

9.3.2.6.1 Place the sample extract into a 125-ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for 1 min with 30-ml portions of hexane-saturated acetonitrile.

9.3.2.6.2 Combine and transfer the acetonitrile phases to a 1-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for about 30 sec. Extract with two 100-ml portions of hexane by vigorously shaking about 15 sec.

9.3.2.6.3 Combine the hexane extracts in a 1-liter separatory funnel and wash with two 100-ml portions of distilled water. Discard the water layer and pour the hexane layer through an 8-10 cm anhydrous sodium sulfate column into a 500-ml Kuderna-Danish flask equipped with a 10-ml ampul. Rinse the separatory funnel and column with three 10-ml portions of hexane.

9.3.2.6.4 Concentrate the extracts to an appropriate volume.

9.3.2.6.5 Analyze as described in Section 10.0.

9.3.2.7 Florisil slurry cleanup

9.3.2.7.1 Place the sample extract into a 20-ml narrow-mouth screw-cap container. Add 0.25 g of Florisil (PR grade or equivalent). Seal with a Teflon-lined screw cap and shake for 1 min.

9.3.2.7.2 Allow the Florisil to settle; then decant the treated solution into a second container with rinsing. Concentrate the sample to an appropriate volume. Analyze as described in Section 10.0.

9.3.2.8 Base cleanup[4]

9.3.2.8.1 Quantitatively transfer the concentrated extract to a 125-ml extraction flask with the aid of several small portions of solvent.

9.3.2.8.2 Evaporate the extract just to dryness with a gentle stream of dry filtered nitrogen, and add 25 ml of 2.5% alcoholic KOH.

9.3.2.8.3 Add a boiling chip, put a water condenser in place, and allow the solution to reflux on a hot plate for 45 min.

9.8.2.8.4 After cooling, transfer the solution to a 250-ml separatory funnel with 25 ml of distilled water.

9.3.2.8.5 Rinse the extraction flask with 25 ml of hexane and add it to the separatory funnel.

9.3.2.8.6 Stopper the separatory funnel and shake vigorously for at least 1 min. Allow the layers to separate, and transfer the lower aqueous phase to a second separatory funnel.

9.3.2.8.7 Extract the saponification solution with a second 25-ml portion of hexane. After the layers have separated, add the first hexane extract to the second separatory funnel and transfer the aqueous alcohol layer to the original separatory funnel.

9.3.2.8.8 Repeat the extraction with a third 25-ml portion of hexane. Discard the saponification solution, and combine the hexane extracts.

9.3.2.8.9 Concentrate the hexane layer to an appropriate volume, and analyze as described in Section 10.0.

10.0 Gas Chromatographic/Electron Impact Mass Spectrometric Determination

10.1 Internal standard addition - An appropriate volume of the internal standard solution is pipetted into the sample. The final concentration of the internal standard must be in the working range of the calibration and well above the matrix background. The internal standard is thoroughly incorporated by mechanical agitation.

Note: The volumetric measurement of the internal standard solution is critical to the overall method precision. The analyst must exercise caution that the volume is known to be ±1% or better. Where necessary, calibration of the pipet is recommended.

10.2 Tables 2, and 5 through 8 summarize the recommended operating conditions for analysis. Figure 1 presents an example of a chromatogram.

10.3 While the highest available chromatographic resolution is not a necessary objective of this protocol, good chromatographic performance is recommended. With the high resolution of CGC, the probability that the chromatographic peaks consist of single compounds is higher than with PGC. Thus, qualitative and quantitative data reduction should be more reliable.

10.4 After performance of the system has been certified for the day and all instrument conditions set according to Tables 2, and 5 through 8, inject an aliquot of the sample onto the GC column. If the response for any ion, including surrogates and internal standards, exceeds the working range of the system, dilute the sample and reanalyze. If the responses of surrogates, internal standards, or analytes are below the working range, recheck the system performance. If necessary, concentrate the sample and reanalyze.

10.5 Record all data on a digital storage device (magnetic disk, tape, etc.) for qualitative and quantitative data reduction as discussed below.

11.0 Qualitative Identification

11.1 Selected ion monitoring (SIM) or limited mass scan (LMS) data - The identification of a compound as a given PCB homolog requires that two criteria be met:

11.1.1 (1) The peak must elute within the retention time window set for that homolog (Section 7.5); and (2) the ratio of two ions obtained by SIM (Table 11) or by LMS (Table 12) must match the natural ratio within ±20%. The analyst must search the higher mass windows, in particular M+70, to prevent misidentification of a PCB fragment ion cluster as the parent.

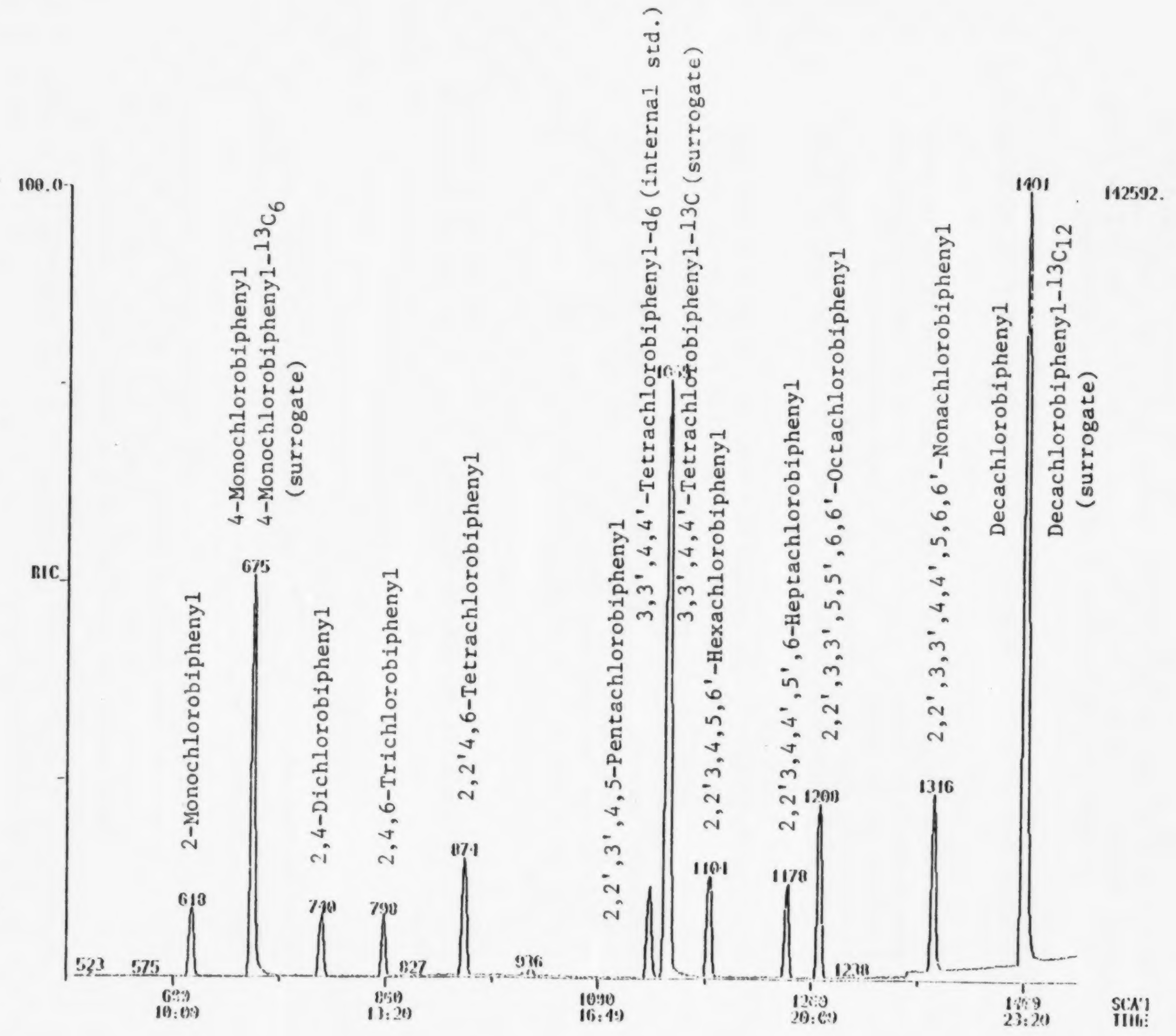

Figure 1. Capillary gas chromatography/electron impact ionization mass spectrometry (CGC/EIMS) chromatogram or the calibration standard solution required for quantitation of PCBs by homolog. This chromatogram includes PCBs representative of each homolog, three carbon-13 labeled surrogates, and the deuterated internal standard. The concentration of all components and the CGC/EIMS parameters are presented in Tables 3, 4, 5, and 7.

TABLE 11. CHARACTERISTIC SIM IONS FOR PCBs

Homolog	Ion (relative intensity)		
	Primary	Secondary	Tertiary
$C_{12}H_9Cl$	188 (100)	190 (33)	-
$C_{12}H_8Cl_2$	222 (100)	224 (66)	226 (11)
$C_{12}H_7Cl_3$	256 (100)	258 (99)	260 (33)
$C_{12}H_6Cl_4$	292 (100)	290 (76)	294 (49)
$C_{12}H_5Cl_5$	326 (100)	328 (66)	324 (61)
$C_{12}H_4Cl_6$	360 (100)	362 (82)	364 (36)
$C_{12}H_3Cl_7$	394 (100)	396 (98)	398 (54)
$C_{12}H_2Cl_8$	430 (100)	432 (66)	428 (87)
$C_{12}HCl_9$	464 (100)	466 (76)	462 (76)
$C_{12}Cl_{10}$	498 (100)	500 (87)	496 (68)

Source: Rote, J. W., and W. J. Morris, "Use of Isotopic Abundance Ratios in Identification of Polychlorinated Biphenyls by Mass Spectrometry," J. Assoc. Offic. Anal. Chem., 56(1), 188-199 (1973).

TABLE 12. LIMITED MASS SCANNING (LMS) RANGES FOR PCBs

Compound	Mass range (m/z)[a]
$C_{12}H_9Cl_1$	186-190
$C_{12}H_8Cl_2$	220-226
$C_{12}H_7Cl_3$	254-260
$C_{12}H_6Cl_3$	288-294
$C_{12}H_5Cl_5$	322-328
$C_{12}H_4Cl_6$	356-364
$C_{12}H_3Cl_7$	386-400
$C_{12}H_2Cl_8$	426-434
$C_{12}HCl_9$	460-468
$C_{12}Cl_{10}$	494-504
$C_{12}D_6Cl_4$	294-300
$^{13}C_6{}^{12}C_6H_9Cl$	192-196
$^{13}C_{12}H_6Cl_4$	300-306
$^{13}C_{12}H_2Cl_8$	438-446
$^{13}C_{12}Cl_{10}$	506-516

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[a] Adapted from Tindall, G. W., and P. E. Wininger, "Gas Chromatography-Mass Spectrometry Method for Identifying and Determining Polychlorinated Biphenyls," J. Chromatogr., 196, 109-119 (1980).

11.1.2 If one or the other of these criteria is not met, interferences may have affected the results, and a reanalysis using full scan EIMS conditions is recommended.

11.2 Full scan data

11.2.1 The peak must elute within the retention time windows set for that homolog (as described in Section 7.5).

11.2.2 The unknown spectrum must match that of an authentic PCB. The intensity of the three largest ions in the molecular cluster (two largest for monochlorobiphenyls) must match the natural ratio within ±20%. Fragment clusters with proper intensity ratios must also be present.

11.2.3 Alternatively, a spectral search may be used to automatically reduce the data. The criteria for acceptable identification include a high index of similarity. For the Incos 2300, a fit of 750 or greater must be obtained.

11.3 Disputes in interpretation - Where there is reasonable doubt as to the identity of a peak as a PCB, the analyst must either identify the peak as a PCB or proceed to a confirmational analysis (see Section 13.0).

12.0 Quantitative Data Reduction

12.1 Once a chromatographic peak has been identified as a PCB, the compound is quantitated based either on the integrated abundance of the SIM data or EICP for the primary characteristic ion in Tables 11 and 12. If interferences are observed for the primary ion, use the secondary and then tertiary ion for quantitation. If interferences in the parent cluster prevent quantitation, an ion from a fragment cluster (e.g., M-70) may be used. Whichever ion is used, the RF must be determined using that ion. The same criteria should be applied to the surrogate compounds (Table 13).

12.2 Using the appropriate analyte-internal standard pair and response factor (RF_p) as determined in Section 7.3, calculate the concentration of each peak using Equation 12-1.

$$\text{Concentration } (\mu g/g) = \frac{A_p}{A_{is}} \cdot \frac{1}{RF_p} \cdot \frac{M_{is}}{M_e} \cdot \frac{V_e}{V_i} \qquad \text{Eq. 12-1}$$

where A_p = area of the characteristic ion for the analyte PCB peak

A_{is} = area of the characteristic ion for the internal standard peak

RF_p = response factor of a given PCB congener

TABLE 13. CHARACTERISTIC IONS FOR ^{13}C-LABELED PCB SURROGATES

Specific compound	Ion (relative intensity)		
	Primary	Secondary	Tertiary
$^{13}C_6{}^{12}C_6H_9Cl$	194 (100)	196 (33)	-
$^{13}C_{12}H_6Cl_4$	304 (100)	306 (49)	302 (78)
$^{13}C_{12}H_2Cl_8$	442 (100)	444 (65)	440 (89)
$^{13}C_{12}Cl_{10}$	510 (100)	512 (87)	514 (50)

M_{is} = mass of internal standard injected (micrograms)

M_e = mass of sample extracted (grams)

V_i = volume injected (microliters)

V_e = volume of sample extract (microliters)

12.3 If a peak appears to contain non-PCB interferences, which cannot be circumvented by a secondary or tertiary ion, either:

12.3.1 Reanalyze the sample on a different column which separates the PCB and interferents;

12.3.2 Perform additional chemical cleanup (Section 9) and then reanalyze the sample; or

12.3.3 Quantitate the entire peak as PCB.

12.4 Calculate the recovery of the four ^{13}C surrogates using the appropriate surrogate-internal standard pair and response factor (RF_{is}) as determined in Section 7.4 using Equation 12-2.

$$\text{Recovery (\%)} = \frac{A_s}{A_{is}} \cdot \frac{1}{RF_s} \cdot \frac{M_{is}}{M_s} \cdot 100 \qquad \text{Eq. 12-2}$$

where A_s = area of the characteristic ion for the surrogate peak

A_{is} = area of the characteristic ion for the internal standard peak

RF_s = response factor for the surrogate compound with respect to the internal standard (Equation 7-2)

M_{is} = mass of internal standard injected (nanograms)

M_s = mass of surrogate, assuming 100% recovery (nanograms)

12.5 Correct the concentration of each peak using Equation 12-3. This is the final reportable concentration.

$$\text{Corrected concentration } (\mu g/g) = \frac{\text{Concentration } \mu g/g}{\text{Recovery (\%)}} \cdot 100 \qquad \text{Eq. 12-3}$$

12.6 Sum all of the peaks for each homolog, and then sum those to yield the total PCB concentration in the sample. Report all numbers in µg/g. The reporting form in Table 14 may be used. If an alternate reporting format (e.g., concentration per peak) is desired, a different report form may be used. The uncorrected concentrations, percent recovery, and corrected recovery are to be reported.

12.7 Round off all numbers reported to two significant figures.

TABLE 14. ANALYSIS REPORT

INCIDENTAL PCBs IN COMMERCIAL PRODUCTS OR PRODUCT WASTES

Sample No. ______________________
Sample Matrix ______________________
Sample Source ______________________
Notebook No. or File Location ________

Volume Extracted _____________ g
Extraction/Cleanup Procedure ____

____

____

Int. Std.	Mass Added (μg)	(Circle one)		Ratio	Intensity
4-Cl(d_6)		298	300	100/49	

Surrogates	Mass Added (μg)	(Circle one)		Ratio	Intensity	% Recovery
1-Cl		194	196	100/33		
4-Cl		304	306	100/49		
8-Cl		442	444	100/65		
10-Cl		510	512	100/87		

(continued)

TABLE 14 (continued)

			Qualitative					Quantitative			
Analyte	1°	2°	I_{1°	I_{2°	Ratio	Theoretical	OK?	Ion Used	RF	Uncorr. Conc. (μg/g)	Corr. Conc. (μg/g)
1-Cl	188	190				100/33					
2-Cl	222	224				100/66					
3-Cl	256	258				100/99					
4-Cl	292	290				100/76					
5-Cl	326	328				100/66					
6-Cl	360	362				100/82					
7-Cl	394	396				100/98					
8-Cl	430	432				100/66					
9-Cl	464	466				100/76					
10-Cl	498	500				100/87					
Total										μg/g Uncorr.	μg/g Corr.

Reported by:	Internal Audit:	EPA Audit:
Name	Name	Name
Signature/Date	Signature/Date	Signature/Date
Organization	Organization	Organization

13.0 Confirmation

If there is reason to question the qualitative identification (Section 11.0), the analyst may choose to confirm that a peak is not a PCB. Any technique may be chosen provided that it is validated as having equivalent or superior selectivity and sensitivity to GC/EIMS. Some candidate techniques include alternate GC columns (with EIMS detection), GC/CIMS, GC/NCIMS, high resolution EIMS, and MS/MS techniques. Each laboratory must validate confirmation techniques to show equivalent or superior selectivity between PCBs and interferences and sensitivity (limit of quantitation, LOQ).

If a peak is confirmed as being a non-PCB, it may be deleted from the calculation (Section 12). If a peak is confirmed as containing both PCB and non-PCB components, it must be quantitated according to Section 12.3.

14.0 Quality Control

14.1 Each laboratory that uses this method must operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory must maintain performance records to define the quality of data that are generated. After a date specified by the Agency, ongoing performance checks should be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

14.2 The analysts must certify that the precision and accuracy of the analytical results are acceptable by:

14.2.1 The absolute precision of surrogate recovery, measured as the RSD_s of the integrated EIMS area (A_s) for a set of samples, must be ±10%.

14.2.2 The mean recovery (R_c) of at least four replicates of a QC check sample to be supplied by the Agency must meet Agency-specified accuracy and precision criteria. This forms the initial data base for establishing control limits (see Section 14.3 below).

14.3 Control limits - The laboratory must establish control limits using the following equations:

Upper control limit (UCL) = $R_c + 3\ RSD_c$

Upper warning limit (UWL) = $R_c + 2\ RSD_c$

Lower warning limit (LWL) = $R_c - 2\ RSD_c$

Lower control limit (LCL) = $R_c - 3\ RSD_c$

These may be plotted on control charts. If an analysis of a check sample falls outside the warning limits, the analyst should be alerted that potential problems may need correction. If the results for a check sample fall outside the control limits, the laboratory must take corrective action and recertify the performance (Section 14.2) before proceeding with analyses. The warning and control limits should be continuously updated as more check sample replicates are added to the data base.

14.4 Before processing any samples, the analyst should demonstrate through the analysis of a reagent blank that all glassware and reagent interferences are under control. Each time a set of samples is analyzed or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against contamination.

14.5 Procedural QC - The various steps of the analytical procedure should have quality control measures. These include but are not limited to:

14.5.1 GC performance - See Section 7.1 for performance criteria.

14.5.2 MS performance - See Section 7.2 for performance criteria.

14.5.3 Qualitative identification - At least 10% of the PCB identifications, as well as any questionable results, should be confirmed by a second mass spectrometrist.

14.5.4 Quantitation - At least 10% of all manual calculations, including peak area calculations, must be checked. After changes in computer quantitation routines, the results should be manually checked.

14.6 A minimum of 10% of all samples, one sample per month or one sample per matrix type, whichever is greater, selected at random, must be run in triplicate to monitor the precision of the analysis. An RSD of ±30% or less must be achieved. If the precision is greater than ±30%, the analyst must be recertified (see Section 14.2).

14.7 A minimum of 10% of all samples, one sample per month or one sample per matrix type, whichever is greater, selected at random, must be analyzed by the standard addition technique. Two aliquots of the sample are analyzed, one "as is" and one spiked (surrogate spiking and equilibration techniques are described in Section 9.2) with a sufficient amount of Solution CSxxx to yield approximately 100 µg/g of each compound. The samples are analyzed together and the quantitative results calculated. The recovery of the spiked compounds (calculated by difference) must be 80-120%. If the sample is known to contain specific PCB isomers, these isomers may be substituted for solution CSxxx. If the concentrations of PCBs are known to be high or low, the amount added should be adjusted so that the spiking level is 1.5 to 4 times the measured PCB level in the unspiked sample.

14.8 Interlaboratory comparison - Interlaboratory comparison studies are planned. Participation requirements, level of performance, and the identity of the coordinating laboratory will be presented in later revisions.

14.9 It is recommended that the participating laboratory adopt additional QC practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates or triplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

15.0 Quality Assurance

Each participating laboratory must develop a quality assurance plan according to EPA guidelines.[5] The quality assurance plan must be submitted to the Agency for approval.

16.0 Method Performance

The method performance is being evaluated. Limits of quantitation; average intralaboratory recoveries, precision, and accuracy; and interlaboratory recoveries, precision, and accuracy will be presented.

17.0 Documentation and Records

Each laboratory is responsible for maintaining full records of the analysis. Laboratory notebooks should be used for handwritten records. GC/MS data must be archived on magnetic tape, disk, or a similar device. Hard copy printouts may be kept in addition if desired. QC records should be maintained separately from sample analysis records.

The documentation must describe completely how the analysis was performed. Any variances from the protocol must be noted and fully described. Where the protocol lists options (e.g., sample cleanup), the option used and specifics (solvent volumes, digestion times, etc.) must be stated.

REFERENCES

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2. Erickson, M. D., and J. S. Stanley, "Methods of Analysis for Incidentally Generated PCBs--Literature Review and Preliminary Recommendations," Interim Report No. 1, EPA Contract No. 68-01-5915, Task 51, 1982.

3. Bellar, T. A., and J. J. Lichtenberg, "The Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils," Prepared for U.S. Environmental Protection Agency, (1981) EPA-600/4-81-045.

4. American Society for Testing and Materials, "Standard Method for Analysis of Environmental Materials for Polychlorinated Biphenyls," pp. 877-885 in Annual Book of ASTM Standards, Part 40, Philadelphia, Pennsylvania (1980). ANSI/ASTM D 3304 - 77.

5. "Quality Assurance Program Plan for the Office of Toxic Substances," Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., October 1980.

APPENDIX C

ANALYTICAL METHOD: THE ANALYSIS OF BY-PRODUCTS CHLORINATED BIPHENYLS IN AIR

THE ANALYSIS OF BY-PRODUCT CHLORINATED BIPHENYLS IN AIR

1.0 Scope and Application

1.1 This is a gas chromatographic/electron impact mass spectrometric (GC/EIMS) method applicable to the determination of chlorinated biphenyls (PCBs) in air emitted from commercial production through stacks, as fugitive emissions, or static (room, other containers, or outside) air. The PCBs present may originate either as synthetic by-products or as contaminants derived from commercial PCB products (e.g., Aroclors). The PCBs may be present as single isomers or complex mixtures and may include all 209 congeners from monochlorobiphenyl through decachlorobiphenyl listed in Table 1.

1.2 The detection and quantitation limits are dependent upon the volume of sample collected, the complexity of the sample matrix and the ability of the analyst to remove interferents and properly maintain the analytical system. The method accuracy and precision will be determined in future studies.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography/mass spectrometry (GC/MS) and in the interpretation of gas chromatograms and mass spectra. Prior to sample analysis, each analyst must demonstrate the ability to generate acceptable results with this method by following the procedures described in Section 14.2.

1.4 The validity of the results depends on equivalent recovery of the analyte and ^{13}C PCBs. If the ^{13}C PCBs are not thoroughly incorporated in the matrix, the method is not applicable.

1.5 During the development and testing of this method, certain analytical parameters and equipment designs were found to affect the validity of the analytical results. Proper use of the method requires that such parameters or designs must be used as specified. These items are identified in the text by the word "must." Anyone wishing to deviate from the method in areas so identified must demonstrate that the deviation does not affect the validity of the data. Alternative test procedure approval must be obtained from the Agency. An experienced analyst may make modifications to parameters or equipment identified by the term "recommended." Each time such modifications are made to the method, the analyst must repeat the procedure in Section 14.2. In this case, formal approval is not required, but the documented data from Sectin 14.2 must be on file as part of the overall quality assurance program.

TABLE 1. NUMBERING OF PCB CONGENERS[a]

No.	Structure
	Monochlorobiphenyls
1	2
2	3
3	4
	Dichlorobiphenyls
4	2,2'
5	2,3
6	2,3'
7	2,4
8	2,4'
9	2,5
10	2,6
11	3,3'
12	3,4
13	3,4'
14	3,5
15	4,4'
	Trichlorobiphenyls
16	2,2',3
17	2,2',4
18	2,2',5
19	2,2',6
20	2,3,3'
21	2,3,4
22	2,3,4'
23	2,3,5
24	2,3,6
25	2,3',4
26	2,3',5
27	2,3',6
28	2,4,4'
29	2,4,5
30	2,4,6
31	2,4',5
32	2,4',6
33	2',3,4
34	2',3,5
35	3,3',4
36	3,3',5
37	3,4,4'
38	3,4,5
39	3,4',5
	Tetrachlorobiphenyls
40	2,2',3,3'
41	2,2',3,4
42	2,2',3,4'
43	2,2',3,5
44	2,2',3,5'
45	2,2',3,6
46	2,2',3,6'
47	2,2',4,4'
48	2,2',4,5
49	2,2',4,5'
50	2,2',4,6
51	2,2',4,6'
	Tetrachlorobiphenyls
52	2,2',5,5'
53	2,2',5,6'
54	2,2',6,6'
55	2,3,3',4
56	2,3,3',4'
57	2,3,3',5
58	2,3,3',5'
59	2,3,3',6
60	2,3,4,4'
61	2,3,4,5
62	2,3,4,6
63	2,3,4',5
64	2,3,4',6
65	2,3,5,6
66	2,3',4,4'
67	2,3',4,5
68	2,3',4,5'
69	2,3',4,6
70	2,3',4',5
71	2,3',4',6
72	2,3',5,5'
73	2,3',5',6
74	2,4,4',5
75	2,4,4',6
76	2',3,4,5
77	3,3',4,4'
78	3,3',4,5
79	3,3',4,5'
80	3,3',5,5'
81	3,4,4',5
	Pentachlorobiphenyls
82	2,2',3,3',4
83	2,2',3,3',5
84	2,2',3,3',6
85	2,2',3,4,4'
86	2,2',3,4,5
87	2,2',3,4,5'
88	2,2',3,4,6
89	2,2',3,4,6'
90	2,2',3,4',5
91	2,2',3,4',6
92	2,2',3,5,5'
93	2,2',3,5,6
94	2,2',3,5,6'
95	2,2',3,5',6
96	2,2',3,6,6'
97	2,2',3',4,5
98	2,2',3',4,6
99	2,2',4,4',5
100	2,2',4,4',6
101	2,2',4,5,5'
102	2,2',4,5,6'
103	2,2',4,5',6
104	2,2',4,6,6'
	Pentachlorobiphenyls
105	2,3,3',4,4'
106	2,3,3',4,5
107	2,3,3',4',5
108	2,3,3',4,5'
109	2,3,3',4,6
110	2,3,3',4',6
111	2,3,3',5,5'
112	2,3,3',5,6
113	2,3,3',5',6
114	2,3,4,4',5
115	2,3,4,4',6
116	2,3,4,5,6
117	2,3,4',5,6
118	2,3',4,4',5
119	2,3',4,4',6
120	2,3',4,5,5'
121	2,3',4,5',6
122	2',3,3',4,5
123	2',3,4,4',5
124	2',3,4,5,5'
125	2',3,4,5,6'
126	3,3',4,4',5
127	3,3',4,5,5'
	Hexachlorobiphenyls
128	2,2',3,3',4,4'
129	2,2',3,3',4,5
130	2,2',3,3',4,5'
131	2,2',3,3',4,6
132	2,2',3,3',4,6'
133	2,2',3,3',5,5'
134	2,2',3,3',5,6
135	2,2',3,3',5,6'
136	2,2',3,3',6,6'
137	2,2',3,4,4',5
138	2,2',3,4,4',5'
139	2,2',3,4,4',6
140	2,2',3,4,4',6'
141	2,2',3,4,5,5'
142	2,2',3,4,5,6
143	2,2',3,4,5,6'
144	2,2',3,4,5',6
145	2,2',3,4,6,6'
146	2,2',3,4',5,5'
147	2,2',3,4',5,6
148	2,2',3,4',5,6'
149	2,2',3,4',5',6
150	2,2',3,4',6,6'
151	2,2',3,5,5',6
152	2,2',3,5,6,6'
153	2,2',4,4',5,5'
154	2,2',4,4',5,6'
155	2,2',4,4',6,6'
156	2,3,3',4,4',5
157	2,3,3',4,4',5'
158	2,3,3',4,4',6
159	2,3,3',4,5,5'
160	2,3,3',4,5,6
	Hexachlorobiphenyls
161	2,3,3',4,5',6
162	2,3,3',4',5,5'
163	2,3,3',4',5,6
164	2,3,3',4',5',6
165	2,3,3',5,5',6
166	2,3,4,4',5,6
167	2,3',4,4',5,5'
168	2,3',4,4',5',6
169	3,3',4,4',5,5'
	Heptachlorobiphenyls
170	2,2',3,3',4,4',5
171	2,2',3,3',4,4',6
172	2,2',3,3',4,5,5'
173	2,2',3,3',4,5,6
174	2,2',3,3',4,5,6'
175	2,2',3,3',4,5',6
176	2,2',3,3',4,6,6'
177	2,2',3,3',4',5,6
178	2,2',3,3',5,5',6
179	2,2',3,3',5,6,6'
180	2,2',3,4,4',5,5'
181	2,2',3,4,4',5,6
182	2,2',3,4,4',5,6'
183	2,2',3,4,4',5',5
184	2,2',3,4,4',6,6'
185	2,2',3,4,5,5',6
186	2,2',3,4,5,6,6'
187	2,2',3,4',5,5',6
188	2,2',3,4',5,6,6'
189	2,3,3',4,4',5,5'
190	2,3,3',4,4',5,6
191	2,3,3',4,4',5',5
192	2,3,3',4,5,5',6
193	2,3,3',4',5,5',6
	Octachlorobiphenyls
194	2,2',3,3',4,4',5,5'
195	2,2',3,3',4,4',5,6
196	2,2',3,3',4,4',5,6'
197	2,2',3,3',4,4',6,6'
198	2,2',3,3',4,5,5',6
199	2,2',3,3',4,5,6,6'
200	2,2',3,3',4,5',6,6'
201	2,2',3,3',4,5,5',6'
202	2,2',3,3',5,5',6,6'
203	2,2',3,4,4',5,5',6
204	2,2',3,4,4',5,6,6'
205	2,3,3',4,4',5,5',6
	Nonachlorobiphenyls
206	2,2',3,3',4,4',5,5',6
207	2,2',3,3',4,4',5,6,6'
208	2,2',3,3',4,5,5',6,6'
	Decachlorobiphenyl
209	2,2',3,3'4,4',5,5',6,5'

[a] Adopted from Ballschmiter, K. and Zell, M., Fresenius Z. Anal.Chem., 302, 20-31 (1980).

2.0 Summary

2.1 The air must be sampled such that the specimen collected for analysis is representative of the whole. Statistically designed selection of the sampling position (stack, flue, port, etc.) or time should be employed. Gaseous and particulate PCBs are withdrawn isokinetically from stacks, room air exhausts, process point exhausts, and other flowing gaseous streams using a sampling train.[1] The PCBs are collected in the Florisil adsorbent tube and in the impingers in front of the adsorbent. PCBs are sampled from ambient air and other static gaseous sources onto a Florisil adsorbent tube. The sample must be preserved to prevent PCB loss prior to analysis. Storage at 4°C is recommended.

2.2 The Florisil adsorbent is extracted with hexane in a Soxhlet extractor, the aqueous condensate is extracted with hexane and the acetone/hexane impinger rinse is back-extracted with water. All three organic extracts are then combined. Optional cleanup techniques may include sulfuric acid cleanup and Florisil adsorption chromatography. The sample is concentrated to a final known volume for instrumental determination.

2.3 The PCB content of the sample extract is determined by capillary (preferred) or packed column gas chromatography/electron impact mass spectrometry (CGC/EIMS or PGC/EIMS) operated in the selected ion monitoring (SIM), full scan, or limited mass scan (LMS) mode.

2.4 PCBs are identified by comparison of their retention time and mass spectral intensity ratios to those in calibration standards.

2.5 PCBs are quantitated against the response factors for a mixture of 11 PCB congeners using the internal standard technique.

2.6 The PCBs identified by the SIM technique may be confirmed by full scan CGC/EIMS, retention on alternate GC columns, other mass spectrometric techniques, infrared spectrometry, or other techniques, provided that the sensitivity and selectivity of the technique are demonstrated to be comparable or superior to GC/EIMS.

2.7 The analysis time is dependent on the extent of workup employed. The time required for instrumental analysis of a single sample excluding data reduction and reporting, is about 30 to 45 min.

2.8 Appropriate quality control (QC) procedures are included to assess the performance of the analyst and estimate the quality of the results. These QC procedures include the demonstration of laboratory capability: periodic analyst certification, the use of control charts, and the analysis of blanks, replicates, and standard addition samples. A quality assurance (QA) plan must be developed for each laboratory.

2.9 While several options are available throughout this method, the recommended procedure for stack gases to be followed is:

2.9.1 The sample is collected using a modified Method 5 train[1] according to a scheme which permits extrapolation of the sample data to the source being assessed.

2.9.2 The sample is preserved at 4°C to prevent any loss of PCBs or changes in matrix which may adversely affect recovery.

2.9.3 The three sample fractions are extracted and combined.

2.9.4 The extract is cleaned up and concentrated to an appropriate volume. Internal standards are added.

2.9.5 An aliquot of the extract is analyzed by CGC/EIMS operated in the SIM mode. On-column injections onto a 15-m DB-5 capillary column, programmed (for toluene solutions) from 110° to 325°C at 10°/min after a 2 min hold is used. Helium at 45-cm/sec linear velocity is used as the carrier gas.

2.9.6 PCBs are identified by retention time and mass spectral intensities.

2.9.7 PCBs are quantitated against the response factors for a mixture of 11 PCB congeners.

2.9.8 The total PCBs are obtained by summing the amounts for each homolog found, and the concentration is reported as micrograms per cubic meter.

3.0 Interferences

3.1 Method interferences may be caused by contaminants, in sample collection media, solvents, reagents, glassware, and other sample processing hardware, leading to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences by the analysis of laboratory reagent blanks as described in Section 14.4.

3.1.1 Glassware must be scrupulously cleaned. All glassware is cleaned as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water and rinses with tap water and reagent water. The glassware should then be drained dry and heated in a muffle furnace at 400°C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After it is dry and cool, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. It is stored inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required. All solvent lots must be checked for purity prior to use.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sorbent material or impingers. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the sources of samples.

4.0 Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemical specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

4.2 Polychlorinated biphenyls have been tentatively classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood. Personnel must wear protective equipment, including gloves and safety glasses.

Congeners highly substituted at the meta and para positions and unsubstituted at the ortho positions are reported to be the most toxic. Extrme caution should be taken when handling these compounds neat or in concentrated solution. The class includes 3,3',4'4'-tetrachlorobiphenyl (both natural abundance and isotopically labeled).

4.3 Waste disposal must be in accordance with RCRA and applicable state rules.

5.0 Apparatus and Materials

All specifications are suggestions only. Catalog numbers and suppliers are included for illustration only.

5.1 Stack sampling train[1] - See Figure 1; a series of four impingers with a solid adsorbent trap between the third and fourth impingers. The train may be constructed by adaptation from a Method 5 train.[2] Descriptions of the train components are contained in the following subsections.

5.1.1 Probe nozzle - Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be ≤ 30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the buttonhook or elbow design, unless otherwise specified by the Agency. The wall thickness of the nozzle shall be less than or equal to that of 20 gauge tubing, i.e., 0.165 cm (0.065 in.) and the distance from the tip of the nozzle to the first bend or point of disturbance shall be at least two times the outside nozzle tubing. Other configurations and construction material may be used with approval from the Agency.

5.1.2 Probe liner - Borosilicate or quartz glass equipped with a connecting fitting that is capable of forming a leak-free, vacuum tight connection without sealing greases; such as Kontes Glass Company "O" ring spherical ground ball joints (model K-671300) or University Research Glassware SVL teflon screw fittings.

A stainless steel (316) or water-cooled probe may be used for sampling high temperature gases with approval from the Agency. A probe heating system may be used to prevent moisture condensation in the probe.

5.1.3 Pitot tube - Type S, or equivalent, attached to probe to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other but not necessarily on the same plane, during sampling. The free space between the nozzle and pitot tube shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3 cm (0.5 in.) ID nozzle, which is the largest size nozzle used.

The pitot tube must also meet the criteria specified in Method 2[2] and be calibrated according to the procedure in the calibration section of that method.

5.1.4 Differential pressure gauge - Inclined manometer capable of measuring velocity head to within 10% of the minimum measured value. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, other methods or devices acceptable to the Agency may be used when conditions warrant.

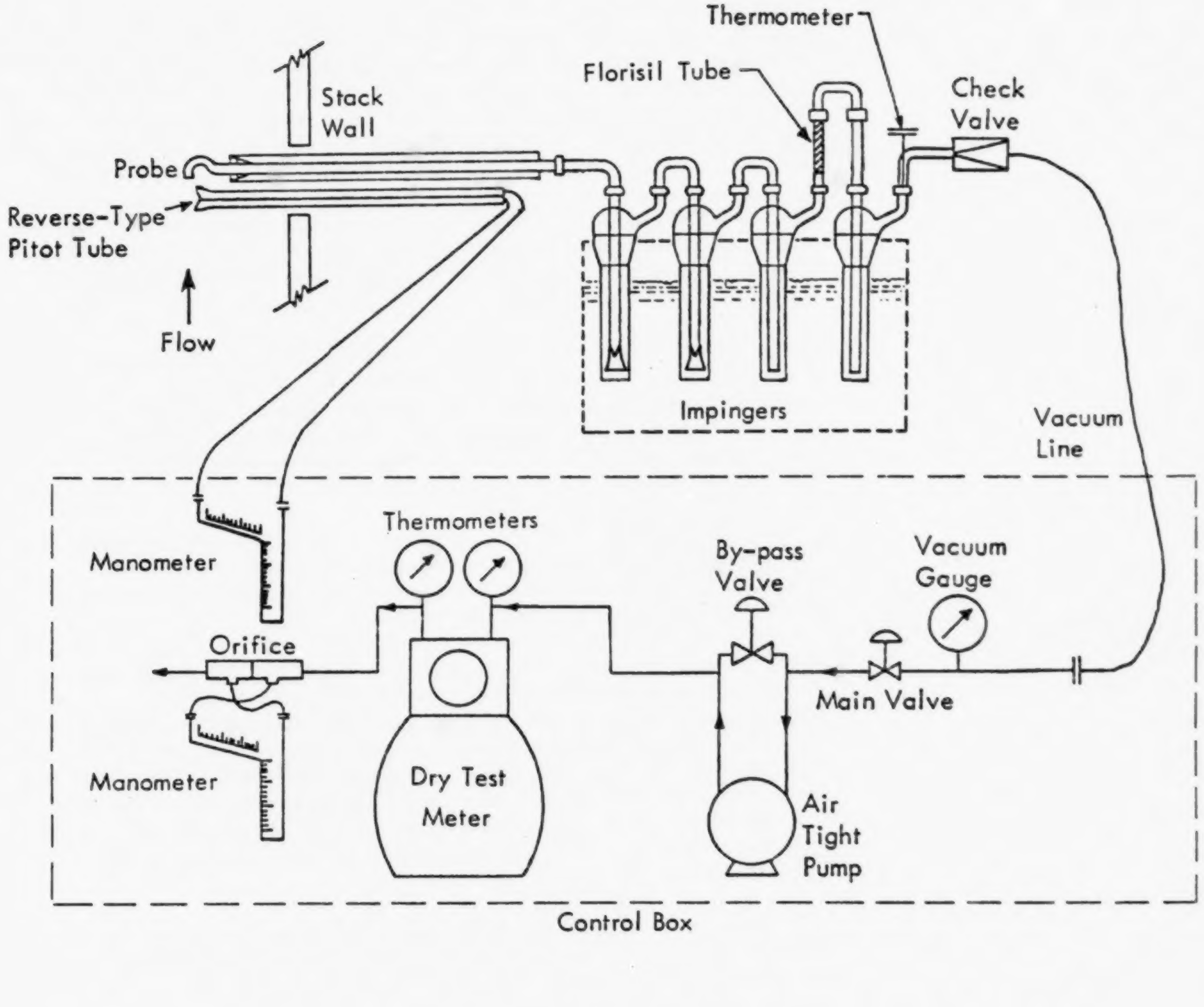
Thermometer
Florisil Tube
Check Valve
Stack Wall
Probe
Reverse-Type Pitot Tube
Flow
Impingers
Vacuum Line
Thermometers
By-pass Valve
Vacuum Gauge
Manometer
Orifice
Main Valve
Manometer
Dry Test Meter
Air Tight Pump
Control Box

Figure 1. PCB sampling train for stack gases.

5.1.5 Impingers - Four impingers with connecting fittings able to form leak-free, vacuum tight seals without sealant greases when connected together as shown in Figure 1. The first and second impingers are of the Greenburg-Smith design. The final two impingers are of the Greenburg-Smith design modified by replacing the tip with a 1.3 cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask.

One or two additional modified Greenburg-Smith impingers may be added to the train between the third impinger and the Florisil tube to accommodate additional water collection when sampling high moisture gases. Throughout the preparation, operation, and sample recovery from the train, these additional impingers should be treated exactly like the third impinger.

5.1.6 Solid adsorbent tube - Glass with connecting fittings able to form leak-free, vacuum tight seals without sealant greases (Figure 2). Exclusive of connectors, the tube has a 2.2 cm inner diameter, is at least 10 cm long, and has four deep indentations on the inlet end to aid in retaining the adsorbent. Ground glass caps (or equivalent) must be provided to seal the adsorbent-filled tube both prior to and following sampling.

5.1.7 Metering system - Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within ±3°C (~ 5°F), dry gas meter with 2% accuracy at the required sampling rate, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

5.1.8 Barometer - Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value shall be requested and an adjustment for elevation differences shall be applied at a rate of -2.5 mm Hg (0.1 in. Hg) per 30 mm (100 ft) elevation increase.

5.2 Static air sampling train[1] - The sampling train, see Figure 3, consists of a glass-lined probe, an adsorbent tube containing Florisil, and the appropriate valving and flow meter controls for isokinetic sampling as described in Section 5.1. The sampling apparatus in Figure 3 is the same as that in Figure 1 and Section 5.1, except that the Smith-Greenburg impingers and heated probe are not used. If condensation of significant quantities of moisture prior to the solid adsorbent is expected, Section 5.1 of the

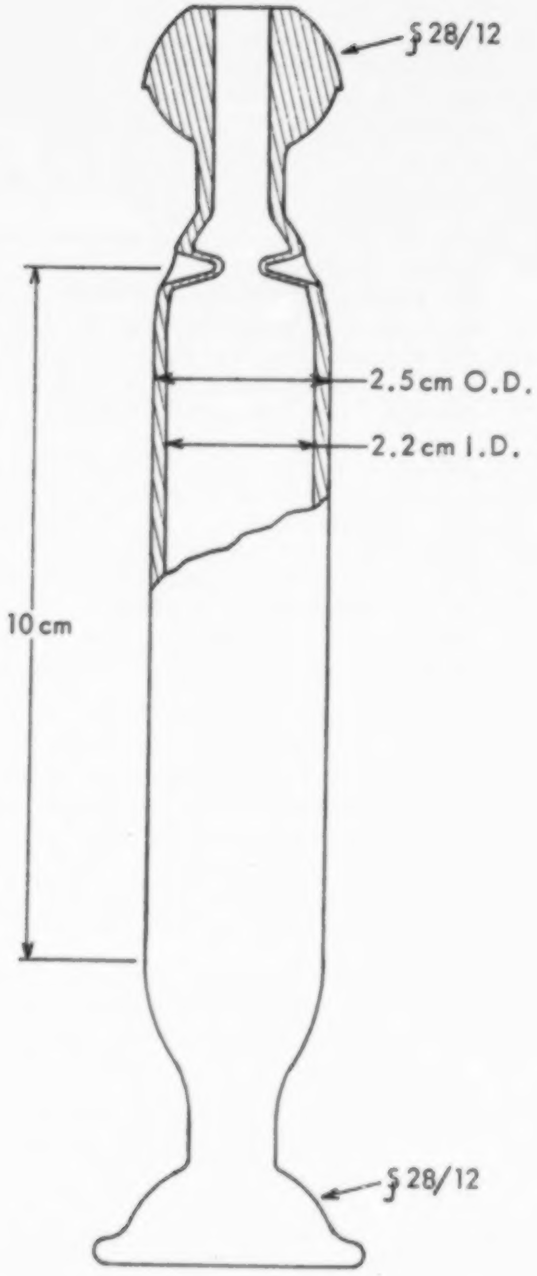
$ 28/12
2.5 cm O.D.
2.2 cm I.D.
10 cm
$ 28/12

Figure 2. Florisil adsorbent tube.

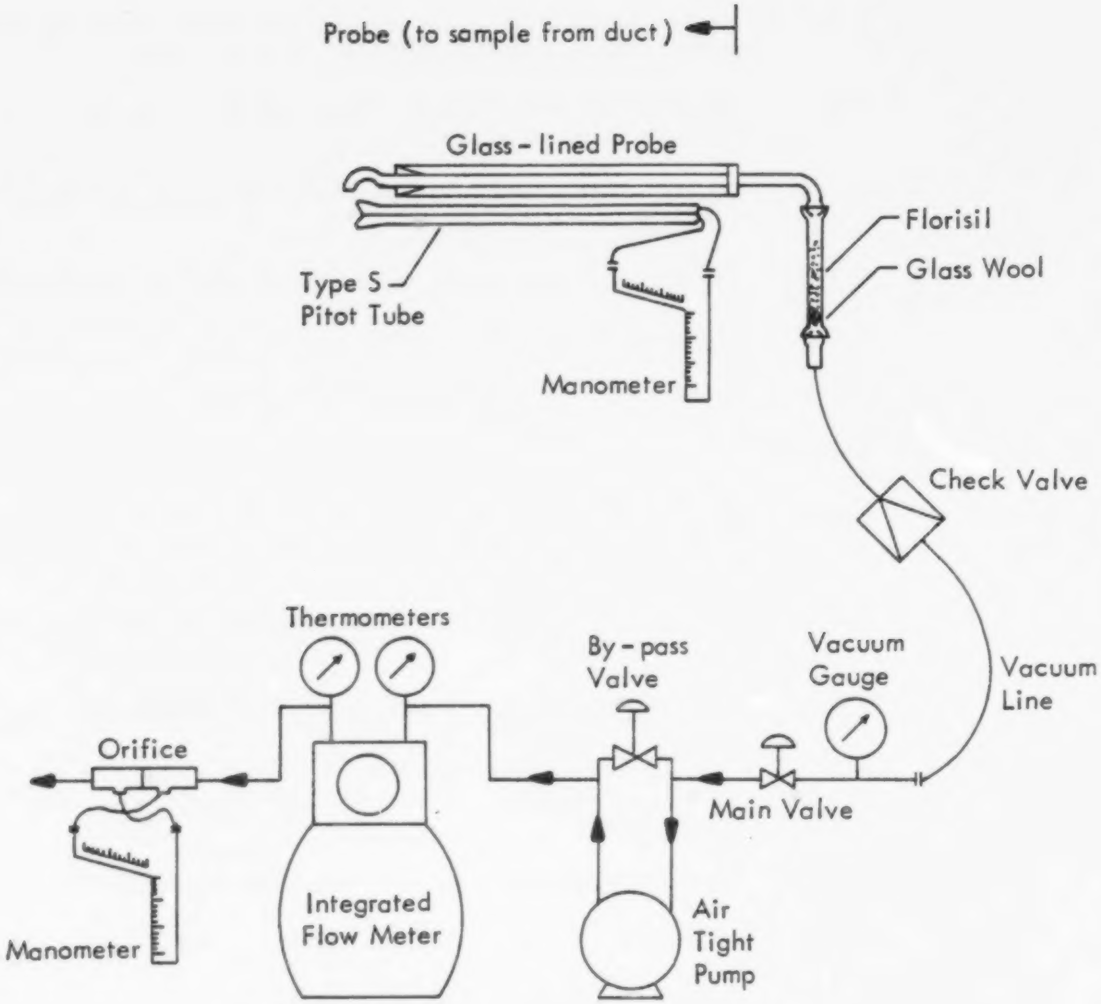
Probe (to sample from duct)
Glass-lined Probe
Florisil
Glass Wool
Type S Pitot Tube
Manometer
Check Valve
Vacuum Line
Thermometers
By-pass Valve
Vacuum Gauge
Orifice
Main Valve
Manometer
Integrated Flow Meter
Air Tight Pump

Figure 3. PCB sampling train for static air.

method should be used. Since probes and adsorbent tubes are not cleaned up in the field, a sufficient number must be provided for sampling and allowance for breakage.

5.3 Sample recovery

5.3.1 Ground glass caps - To cap off adsorbent tube and the other sample exposed portions of the train.

5.3.2 Teflon FEP® wash bottle - Two, 500 ml, Nalgene No. 0023A59 or equivalent.

5.3.3 Sample storage containers - Glass bottles, 1 liter, with TFE®-lined screw caps.

5.3.4 Balance - Triple beam, Ohaus Model 7505 or equivalent.

5.3.5 Aluminum foil - Heavy duty.

5.3.6 Metal can - To recover used silica gel.

5.4 Analysis

5.4.1 Glass Soxhlet extractors - 40 mm ID complete with 45/50 \$ condenser, 24/40 \$ 250 ml round-bottom flask, heating mantle for 250 ml flask, and power transformer.

5.4.2 Teflon FEP wash bottle - Two, 500 ml, Nalgene No. 0023A59 or equivalent.

5.4.3 Separatory funnel - 1,000 ml with TFE® stopcock.

5.4.4 Kuderna-Danish concentrators - 500 ml.

5.4.5 Steam bath.

5.4.6 Separatory funnel - 50 ml with TFE® stopcock.

5.4.7 Volumetric flask - 25.0 ml, glass.

5.4.8 Volumetric flask - 5.0 ml, glass.

5.4.9 Culture tubes - 13 x 100 mm, glass with TFE®-lined screw caps.

5.4.10 Pipette - 5.0 ml glass.

5.4.11 Teflon®-glass syringe - 1 ml, Hamilton 1001 TLL or equivalent with Teflon® needle.

5.4.12 Syringe - 10 µl, Hamilton 701N or equivalent.

5.4.13 Disposable glass pipettes with bulbs - To aid transfer of the extracts.

5.4.14 Gas chromatography/mass spectrometer system.

5.4.14.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using capillary columns or packed columns. Other capillary injection techniques (split, splitless, "Grob," etc.) may be used provided the performance specifications stated in Section 7.1 are met.

5.4.14.2 Capillary GC column - A 12-20 m long x 0.25 mm ID fused silica column with a 0.25 µm thick DB-5 bonded silicone liquid phase (J&W Scientific) is recommended. Alternate liquid phases may include OV-101, SP-2100, Apiezon L, Dexsil 300, or other liquid phases which meet the performance specifications stated in Section 7.1.

5.4.14.3 Packed GC column - A 180 cm x 0.2 cm ID glass column packed with 3% SP-2250 on 100/120 mesh Supelcoport or equivalent is recommended. Other liquid phases which meet the performance specifications stated in Section 7.1 may be substituted.

5.4.14.4 Mass spectrometer - Must be capable of scanning from 150 to 550 daltons every 1.5 sec or less, collecting at least five spectra per chromatographic peak, utilizing a 70-eV (nominal) electron energy in the electron impact ionizaton mode and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of decafluorotriphenyl phosphine [DFTPP, bis(perfluorophenyl)phenyl phosphine] is injected through the GC inlet. Any GC-to-MS interface that gives acceptable calibration points at 10 ng per injection for each PCB isomer in the calibration standard and achieves all acceptable performance criteria (Section 10) may be used. Direct coupling of the fused silica column to the MS is recommended. Alternatively, GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

TABLE 2. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion abundance criteria
197	Less than 1% of mass 198
198	100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present, but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

5.4.14.5 A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The data system must have the capability of integrating the abundances of the selected ions between specified limits and relating integrated abundances to concentrations using the calibration procedures described in this method. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number to yield an extracted ion current profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

6.0 Reagents

6.1 Sampling

6.1.1 Florisil - Floridin Company, 30/60 mesh, Grade A. The Florisil is cleaned by 8 hr Soxhlet extraction with hexane and then by drying for 8 hr in an oven at 110°C and is activated by heating to 650°C for 2 hr (not to exceed 3 hr) in a muffle furnace. After allowing to cool to near 110°C transfer the clean, active Florisil to a clean, hexane-washed glass jar and seal with a TFE®-lined lid. The Florisil should be stored at 110°C until taken to the field for use. Florisil that has been stored more than 1 month must be reactivated before use.

6.1.2 Glass wool - Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

6.1.3 Water - Deionized, then glass-distilled, and stored in hexane-rinsed glass containers with TFE®-lined screw caps.

6.1.4 Silica gel - Indicating type, 6-16 mesh. If previously used, dry at 175°C for 2 hr. New silica gel may be used as received.

6.1.5 Crushed ice.

6.2 Solvents - All solvents must be pesticide residue analysis grade. New lots should be checked for purity by concentrating an aliquot by at least as much as is used in the procedure.

6.3 Calibration standard congeners - Standards of the PCB congeners listed in Table 3 are available from Ultra Scientific, Hope, Rhode Island; or Analabs, North Haven, Connecticut.

6.4 Calibration standard stock solutions - Primary dilutions of each of the individual PCBs listed in Table 3 are prepared by weighing approximately 1-10 mg of material within 1% precision. The PCB is then dissolved and diluted to 1.0 ml with hexane. The concentration is calculated in mg/ml. The primary dilutions are stored at 4°C in screw-cap vials with Teflon cap liners. The meniscus is marked on the vial wall to monitor solvent evaporation. Primary dilutions are stable indefinitely if the seals are maintained. The validity of primary and secondary dilutions must be monitored on a quarterly basis by analyzing four quality control check samples (see Section 14.2).

6.5 Working calibration standards - Working calibration standards are prepared that are similar in PCB composition and concentration to the samples by mixing and diluting the individual standard stock solutions. Example calibration solutions are shown in Table 3. The mixture is diluted to volume with pesticide residue analysis quality hexane. The concentration is calculated in ng/ml as the individual PCBs. Dilutions are stored at 4°C in narrow-mouth, screw-cap vials with Teflon cap liners. The meniscus is marked on the vial wall to monitor solvent evaporation. These secondary dilutions can be stored indefinitely if the seals are maintained. These solutions are designated "CSxxx," where the xxx is used to encode the nominal concentration in ng/ml.

6.6 Alternatively, certified stock solutions similar to those listed in Table 3 may be available from a supplier, in lieu of the procedures described in Section 6.4.

6.7 DFTPP standard - A 50 ng/µl solution of DFTPP is prepared in acetone or another appropriate solvent.

6.8 Internal standard stock solution - The four ^{13}C-labeled PCBs listed in Table 4 may be available from a supplier as a certified solution. This solution may be used as received or diluted further.

6.9 Solution stability - The calibration standard, surrogate and DFTPP solutions should be checked frequently for stability. These solutions should be replaced after 6 months, or sooner if comparison with quality control check samples indicates compound degradation or concentration change.

6.10 Quality control check samples will be supplied by the Agency.

TABLE 3. CONCENTRATIONS OF CONGENERS IN PCB CALIBRATION STANDARDS (ng/ml)[a]

Homolog	Congener no.	CS1000	CS100	CS050	CS010
1	1	1,040	104	52	10
1	3	1,000	100	50	10
2	7	1,040	104	52	10
3	30	1,040	104	52	10
4	50	1,520	152	76	15
5	97	1,740	174	87	17
6	143	1,920	192	96	19
7	183	2,600	260	130	26
8	202	4,640	464	232	46
9	207	5,060	506	253	51
10	209	4,240	424	212	42
4	210 (IS)	255	255	255	255
1	211 (RS)	104	104	104	104
4	212 (RS)	257	257	257	257
8	213 (RS)	407	407	407	407
10	214 (RS)	502	502	502	502

[a] Concentrations given as examples only.

TABLE 4. COMPOSITION OF INTERNAL STANDARD SPIKING SOLUTION (SS100) CONTAINING ^{13}C-LABELED PCBs[a]

Congener no.	Compound	Concentration (μg/ml)
211	(1',2',3',4',5',6'-$^{13}C_6$)4-chlorobiphenyl	104
212	($^{13}C_{12}$)3,3',4,4'-tetrachlorobiphenyl	257
213	($^{13}C_{12}$)2,2',3,3',5,5',6,6'-octachlorobiphenyl	395
214	($^{13}C_{12}$)decachlorobiphenyl	502

[a] Concentrations given as examples only.

7.0 Calibration

Maintain a laboratory log of all calibrations.

7.1 Sampling train

7.1.1 Probe nozzle - Using a micrometer, the inside diameter of the nozzle is measured to the nearest 0.025 mm (0.001 in.). Three separate measurements are made using different diameters each time and obtain the average of the measurements. The difference between the high and low numbers must not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they must be reshaped, sharpened, and recalibrated before use.

Each nozzle must be permanently and uniquely identified.

7.1.2 Pitot tube - The pitot tube must be calibrated according to the procedure outlined in Method 2.[2]

7.1.3 Dry gas meter and orifice meter - Both meters must be calibrated according to the procedure outlined in APTD-0581.[3] When diaphragm pumps with bypass valves are used, proper metering system design is checked by calibrating the dry gas meter at an additional flow rate of 0.0057 m^3/min (0.2 cfm) with the bypass valve fully opened and then with it fully closed. If there is more than ±2% difference in flow rates when compared to the fully closed position of the bypass valve, the system is not designed properly and must be corrected.

7.1.4 Probe heater calibration - The probe heating system must be calibrated according to the procedure contained in APTD-0581.[3]

7.1.5 Temperature gauges - Dial and liquid filled bulb thermometers are calibrated against mercury-in-glass thermometers. Thermocouples should be calibrated in constant temperature baths.

7.2 The gas chromatograph must meet the minimum operating parameters shown in Tables 5 and 6, daily. If all of the criteria are not met, the analyst must adjust conditions and repeat the test until all criteria are met.

7.3 The mass spectrometer must meet the minimum operating parameters shown in Tables 2, 7, and 8, daily. If all criteria are not met, the analyst must retune the spectrometer and repeat the test until all conditions are met.

TABLE 5. OPERATING PARAMETERS FOR CAPILLARY COLUMN GAS CHROMATOGRAPHIC SYSTEM

Parameter	Recommended	Tolerance
Gas chromatograph	Finnigan 9610	Other[a]
Column	15 m x 0.255 mm ID Fused silica	Other
Liquid phase	DB-5 (J&W)	Other nonpolar or semipolar
Liquid phase thickness	0.25 μm	< 1 μm
Carrier gas	Helium	Hydrogen
Carrier gas velocity	45 cm/sec[b]	Optimum performance
Injector	On-column (J&W)[c]	Other
Injector temperature	Optimum performance[c]	Optimum performance
Injection volume	1.0 μl[c]	Other
Initial column temperature	70°C (2 min)[d]	Other
Column temperature program	70°-325°C at 10°C/min[e]	Other
Separator	None[f]	Glass jet or other
Transfer line temperature	280°C	Optimum[g]
Tailing factor[h]	0.7-1.5	0.4-3
Peak width[i]	7-10 sec	< 15 sec

[a] Substitutions permitted with any common apparatus or technique provided performance criteria are met.

[b] Measured by injection of air or methane at 270°C oven temperature.

[c] For on-column injection, manufacturer's instructions should be followed regarding injection technique.

[d] With on-column injection, initial temperature equals boiling point of the solvent; in this instance, hexane.

[e] $C_{12}Cl_{10}$ elutes at 270°C. Programming above this temperature ensures a clean column and lower background on subsequent runs.

[f] Fused silica columns may be routed directly into the ion source to prevent separator discrimination and losses.

[g] High enough to elute all PCBs, but not high enough to degrade the column if routed through the transfer line.

[h] Tailing factor is width of front half of peak at 10% height divided by width of back half of peak at 10% height for single PCB congeners in solution CSxxx.

[i] Peak width at 10% height for a single PCB congener is CSxxx.

TABLE 6. OPERATING PARAMETERS FOR PACKED COLUMN GAS CHROMATOGRAPHY SYSTEM

Parameter	Recommended	Tolerance
Gas chromatograph	Finnigan 9610	Other[a]
Column	180 cm x 0.2 cm ID glass	Other
Column packing	3% SP-2250 on 100/120 mesh Supelcoport	Other nonpolar or semipolar
Carrier gas	Helium	Hydrogen
Carrier gas flow rate	30 ml/min	Optimum performance
Injector	On-column	Other
Injector temperature	250°C	Optimum[b]
Injection volume	1.0 μl	≦ 5 μl
Initial column temperature	150°C, 4 min	Other
Column temperature program	150°-260°C at 8°/min	Other
Separator	Glass jet	Other
Transfer line temperature	280°C	Optimum[a]
Tailing factor[c]	0.7-1.5	0.4-3
Peak width[d]	10-20 sec	< 30 sec

---

[a] Substitutions permitted if performance criteria are met.

[b] High enough to elute all PCBs.

[c] Tailing factor is width of front half of peak at 10% height divided by width of back half of peak at 10% height for single PCB congeners in solution CSxxx.

[d] Peak width at 10% height for a single PCB congener is CSxxx.

TABLE 7. OPERATING PARAMETERS FOR QUADRUPOLE MASS SPECTROMETER SYSTEM

Parameter	Recommended	Tolerance
Mass spectrometer	Finnigan 4023	Other[a]
Data system	Incos 2400	Other
Scan range	95-550	Other
Scan time	1 sec	Other[b]
Resolution	Unit	Optimum performance
Ion source temperature	280°C	200°-300°C
Electron energy[c]	70 eV	Optimum performance
Trap current	0.2 mA	Optimum performance
Multiplier voltage	-1,600 V	Optimum performance
Preamplifier sensitivity	10^{-6} A/V	Set for desired working range

---

[a] Substitutions permitted if performance criteria are met.

[b] Greater than five data points over a GC peak is a minimum.

[c] Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no separator is used.

TABLE 8. OPERATING PARAMETERS FOR MAGNETIC SECTOR MASS SPECTROMETER SYSTEM

Parameter	Recommended	Tolerance
Mass spectrometer	Finnigan MAT 311A	Other[a]
Data system	Incos 2400	Other
Scan range	98-550	Other
Scan mode	Exponential	Other
Cycle time	1.2 sec	Other[b]
Resolution	1,000	> 500
Ion source temperature	280°C	250-300°
Electron energy[c]	70 eV	70 eV
Emission current	1-2 mA	Optimum
Filament current	Optimum	Optimum
Multiplier	-1,600 V	Optimum

[a] Substitutions permitted if performance criteria are met.

[b] Greater than five data points over a GC peak is a minimum.

[c] Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no separator is used.

7.4 The PCB response factors (RF_p) must be determined using Equation 7-1 for the analyte homologs:

$$RF_p = \frac{A_p \times M_{is}}{A_{is} \times M_p} \qquad \text{Eq. 7-1}$$

where RF_p = response factor of a given PCB isomer

A_p = area of the characteristic ion for the PCB congener peak

M_p = mass of PCB congener injected (nanograms)

A_{is} = area of the characteristic ion for the internal standard peak

M_{is} = mass of internal standard injected (nanograms)

If specific congeners are known to be present and if standards are available, selected RF values may be employed. For general samples, solutions CSxxx and SSxxx or a mixture (Tables 3 and 4) may be used as the response factor solution. The PCB-surrogate pairs to be used in the RF calculation are listed in Table 9.

Generally, only the primary ions of both the analyte and surrogate are used to determine the RF values. If alternate ions are to be used in the quantitation, the RF must be determined using that characteristic ion.

The RF value must be determined in a manner to assure ±20% accuracy and precision. For instruments with good day-to-day precision, a running mean ($\overline{RF}$) based on seven values determined once each day may be appropriate. Other options include, but are not limited to, triplicate determinations of a single concentration spaced throughout a day or determination of the RF at three different levels to establish a working curve.

If replicate RF values differ by greater than ±10% RSD, the system performance should be monitored closely. If the RSD is greater than ±20%, the data set must be considered invalid and the RF redetermined before further analyses are done.

7.5 If the GC/EIMS system has not been demonstrated to yield a linear response or if the analyte concentrations are more than one order of magnitude different from those in the RF solution, a calibration curve must be prepared. If the analyte and RF solution concentrations differ by more than one order of magnitude, a calibration curve should be prepared. A calibration curve should be established with triplicate determinations at three or more concentrations bracketing the analyte levels.

TABLE 9. PAIRINGS OF ANALYTE, CALIBRATION, AND SURROGATE COMPOUNDS

Analyte		Calibration standard		Surrogate	
Congener[a] no.	Compound	Congener no.	Compound	Congener no.	Compound
1	2-$C_{12}H_9Cl$	1	2	211	$^{13}C_6$-4
2,3	3- and 4-$C_{12}H_9Cl$	3	4	211	$^{13}C_6$-4
4-15	$C_{12}H_8Cl_2$	7	2,4	211	$^{13}C_6$-4
16-39	$C_{12}H_7Cl_3$	30	2,4,6	212	$^{13}C_{12}$-3,3',4,4'
40-81	$C_{12}H_6Cl_4$	50	2,2',4,6	212	$^{13}C_{12}$-3,3',4,4'
82-127	$C_{12}H_5Cl_5$	97	2,2',3',4,5	212	$^{13}C_{12}$-3,3',4,4'
128-169	$C_{12}H_4Cl_6$	143	2,2',3,4,5,6'	212	$^{13}C_{12}$-3,3',4,4'
170-193	$C_{12}H_3Cl_7$	183	2,2',3',4,4',5',6	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
194-205	$C_{12}H_2Cl_8$	202	2,2',3,3',5,5',6,6'	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
206-208	$C_{12}HCl_9$	207	2,2',3,3',4,4',5,6,6'	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
209	$C_{12}Cl_{10}$	209	$C_{12}Cl_{10}$	214	$^{13}C_{12}Cl_{10}$

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[a] Ballschmiter numbering system, see Table 1.

7.6 The relative retention time (RRT) windows for the 10 homologs and surrogates must be determined. If all congeners are not available, a mixture of available congeners or an Aroclor mixture (e.g., 1016/1254/1260) may be used to estimate the windows. The windows must be set wider than observed if all isomers are not determined. Typical RRT windows for one column are listed in Table 10. The windows may differ substantially if other GC parameters are used.

8.0 Sample Collection, Handling, and Preservation

The sampling shall be conducted by competent personnel experienced with this test procedure and cognizant of the constraints of the anaytical techniques for PCBs, particularly contamination problems.

8.1 Stack sampling[1]

8.1.1 Pretest preparation - All train components shall be maintained and calibrated according to the procedure described in APTD-0581,[3] unless otherwise specified herein. This should be done in the laboratory prior to sampling.

8.1.1.1 Cleaning glassware - All glass parts of the train upstream of and including the adsorbent tube and impingers, should be cleaned as described in Section 3.1.1. Special care should be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. These grease residues should be removed by soaking several hours in a chromic acid cleaning solution prior to routine cleaning as described above.

8.1.1.2 Solid adsorbent tube - 7.5 g of Florisil activated within the last 30 days and still warm from storage in a 110°C oven, is weighed into the adsorbent tube (prerinsed with hexane) with a glass wool plug in the downstream end. A second glass wool plug is placed in the tube to hold the sorbent in the tube. Both ends of the tube are capped with ground glass caps. These caps should not be removed until the tube is fitted to the train immediately prior to sampling.

8.1.2 Preliminary determinations - The sampling site and the minimum number of sampling points are selected according to Method 1[2] or as specified by the Agency. The stack pressure, temperature, and the range of velocity heads are determined using Method 2[2] and moisture content using Approximation Method 4[2] or its alternatives for the purpose of making isokinetic sampling rate calculations. Estimates may be used. However, final results must be based on actual measurements made during the test.

TABLE 10. RELATIVE RETENTION TIME (RRT) RANGES OF PCB HOMOLOGS VERSUS d_6-3,3',4,4'-TETRACHLOROBIPHENYL

PCB homolog	No. of isomers measured	Observed range of RRTs[a]	Congener no.	Observed RRT[a]	Projected range of RRTs[b]
Monochloro	3	0.40-0.50	1 3	0.43 0.50	0.35-0.55
Dichloro	10	0.52-0.69	7	0.58	0.35-0.80
Trichloro	9	0.62-0.79	30	0.65	0.35-0.10
Tetrachloro	16	0.72-1.01	50	0.75	0.55-1.05
Pentachloro	12	0.82-1.08	97	0.98	0.80-1.10
Hexachloro	13	0.93-1.20	143	1.05	0.90-1.25
Heptachloro	4	1.09-1.30	183	1.15	1.05-1.35
Octachloro	6	1.19-1.36	202	1.19	1.10-1.50
Nonachloro	3	1.31-1.42	207	1.33	1.25-1.50
Decachloro	1	1.44-1.45	209	1.44	1.35-1.50

[a] The RRTs of the 77 congeners and a mixture of Aroclor 1016/1254/1260 were measured versus 3,3',4,4'-tetrachlorobiphenyl-d_6 (internal standard) using a 15-m J&W DB-5 fused silica column with a temperature program of 110°C for 2 min, then 10°C/min to 325°C, helium carrier at 45 cm/sec, and an on-column injector. A Finnigan 4023 Incos quadrupole mass spectrometer operating with a scan range of 95-550 daltons was used to detect each PCB congener.

[b] The projected relative retention windows account for overlap of eluting homologs and take into consideration differences in operating systems and lack of all possible 209 PCB congeners.

The molecular weight of the stack gases is determined using Method 3.[2]

A nozzle size is selected based on the maximum velocity head so that isokinetic sampling can be maintained at a rate less than 0.75 cfm. It is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, the nozzle size must not be changed.

A suitable probe length is selected such that all traverse points can be sampled. Sampling from opposite sides for large stacks may be considered to reduce the length of probes.

A sampling time is selected appropriate for total method sensitivity and the PCB concentration anticipated. Sampling times should generally fall within a range of 2 to 4 hr.

A buzzer-timer should be incorporated in the control box (see Figure 1) to alarm the operator to move the probe to the next sampling point.

8.1.3 Preparation of collection train - During preparation and assembly of the sampling train, all train openings must be covered until just prior to assembly or until sampling is about to begin. Immediately prior to assembly, all parts of the train upstream of the adsorbent tube are rinsed with hexane. The probe is marked with heat resistant tape or by some other method at points indicating the proper distance into the stack or duct for each sampling point.

200 ml of water is placed in each of the first two impingers, and the third impinger left empty. CAUTION: Sealant greases must not be used in assembling the train. If the preliminary moisture determination shows that the stack gases are saturated or supersaturated, one or two additional empty impingers should be added to the train between the third impinger and the Florisil tube. See Section 5.1.5. Approximately 200 to 300 g or more, if necessary, of silica gel is placed in the last impinger. Each impinger (stem included) is weighed and the weights recorded to the nearest 0.1 g on the impingers and on the data sheet.

Unless otherwise specified by the Agency, a temperature probe is attached to the metal sheath of the sampling probe so that the sensor is at least 2.5 cm behind the nozzle and pitot tube and does not touch any metal.

The train is assembled as shown in Figure 1. Through all parts of this method use of sealant greases such as stopcock grease to seal ground glass joints must be avoided.

Crushed ice is placed around the impingers.

8.1.4 Leak check procedure - After the sampling train has been assembled, the probe heating system(s) is turned on and set (if applicable) to reach a temperature sufficient to avoid condensation in the probe. Time is allowed for the temperature to stabilize. The train is leak checked at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum. A leakage rate in excess of 4% of the average sampling rate or 0.0057 m^3/min (0.02 cfm) whichever is less, is unacceptable.

The following leak check instruction for the sampling train described in APTD-0581[3] may be helpful. The pump is started with bypass valve fully open and coarse adjust valve completely closed. The coarse adjust valve is partially opened and the bypass valve slowly closed until 380 mm Hg (15 in. Hg) vacuum is reached. The direction of bypass valve must not be reversed. This will cause water to back up into the probe. If 380 mm Hg (15 in. Hg) is exceeded, either the leak check is conducted at this higher vacuum or the leak check is ended as described below and start over.

When the leak check is completed, the plug is first slowly removed from the inlet to the probe and the vacuum pump is immediately turned off. This prevents the water in the impingers from being forced backward into the probe.

Leak checks shall be conducted as described above prior to each test run and at the completion of each test run. If leaks are found to be in excess of the acceptable rate, the test will be considered invalid. To reduce lost time due to leakage occurrences, it is recommended that leak checks be conducted between port changes.

8.1.5 Train operation - During the sampling run, an isokinetic sampling rate within 10%, or as specified by the Agency, of true isokinetic shall be maintained. During the run, the nozzle or any other part of the train in front of and including the Florisil tube must not be changed.

For each run, the data required on the data sheets must be recorded. An example is shown in Figure 4. The dry gas meter readings are recorded at the beginning and end of each sampling time increment, when changes in flow rates are made, and when sampling is halted. Other data point readings are taken at least once at each sample point during each time increment and whenever significant

FIELD DATA

PLANT __________
DATE __________
SAMPLING LOCATION __________
SAMPLE TYPE __________
RUN NUMBER __________
OPERATOR __________
AMBIENT TEMPERATURE __________
BAROMETRIC PRESSURE __________
STATIC PRESSURE, (P_s) __________
FILTER NUMBER (s) __________

PROBE LENGTH AND TYPE __________
NOZZLE I.D. __________
ASSUMED MOISTURE, % __________
SAMPLE BOX NUMBER __________
METER BOX NUMBER __________
METER $\Delta H_@$ __________
C FACTOR __________
PROBE HEATER SETTING __________
HEATER BOX SETTING __________
REFFERENCE Δp __________

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY ______ MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (24-hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
				DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F			

COMMENTS

Figure 4. Field data sheet.

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changes (20% variation in velocity head readings) necessitate additional adjustments in flow rate.

The portholes are cleaned prior to the test run to minimize change of sampling deposited material. To begin sampling, the nozzle cap is removed, the probe heater operational and temperature up, and the pitot tube and probe positions are verified (if applicable). The nozzle is positioned at the first traverse point with the tip pointing directly into the gas stream. The pump is started and the flow adjusted to isokinetic conditions. Nomographs are available for sampling trains using type S pitot tubes with 0.85 ± 0.02 coefficients (C_p), and when sampling in air or a stack gas with equivalent density (molecular weight, M_d, equal to 29 ± 4), which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. If C_p and M_d are outside the above stated ranges, the nomograph cannot be used unless appropriate steps are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), the coarse adjust valve must be closed before inserting the probe into the stack to avoid water backing into the probe. If necessary, the pump may be turned on with the coarse valve closed.

When the probe is in position, the openings around the probe and porthole must be blocked off to prevent unrepresentative dilution of the gas stream.

The stack cross section is traversed, as required by Method 1[2] or as specified by the Agency. To minimize chance of extracting deposited material, the probe nozzle should not bump into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes.

During the test run, periodic adjustments are made to keep the probe temperature at the proper value. More ice and, if necessary, salt is added to the ice bath to maintain a temperature of less than 20°C (68°F) at the impinger/silica gel outlet, to avoid excessive moisture losses. Also, the level and zero of the manometer should be periodically checked.

If the pressure drop across the train becomes high enough to make isokinetic sampling difficult to maintain, the test run should be terminated. Under no circumstances should the train be disassembled during the test run to determine and correct causes of excessive pressure drops.

At the end of the sample run, the pump is turned off, the probe and nozzle removed from the stack, and the final dry gas meter reading recorded. A leak check is performed, with acceptability of the test run based on the same criteria as in Section 8.1.4. The percent isokinetic is calculated (see calculation section) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, the Agency should be consulted for possible variance on the isokinetic rates.

8.1.6 Blank train - For each series of test runs, a blank train is set up in a manner identical to that described above, but with the nozzle capped with aluminum foil and the exit end of the last impinger capped with a ground glass cap. The train is allowed to remain assembled for a period equivalent to one test run. The blank sample is recovered as described in Section 8.3.

8.2 Static air sampling[3] - The sampling procedure for static air is identical to that described in Section 8.1 with the following exceptions: (a) impingers and a heatable probe are not required prior to the adsorbent tube; and (b) the PCB concentrations may dictate a longer or shorter sampling time.

The selection of sampling time and rate should be based on the approximate levels of PCB residues expected in the sample. The sampling rate should not exceed 14 liter/min and may typically fall in the range of 5 to 10 liter/min. Sampling times should be more than 20 min but should not exceed 4 hr.

8.3 Sample recovery - Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safely handled, all external particulate matter near the tip of the probe nozzle is wiped off. The probe is removed from the train and both ends closed off with aluminum foil. The inlet to the train is capped off with a ground glass cap.

The probe and impinger assembly are transfered to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

The train is inspected prior to and during disassembly and any abnormal conditions noted. The samples are treated as follows:

8.3.1 Adsorbent tube - The Florisil tube is removed from the train and capped with ground glass caps.

8.3.2 Sample Container No. 1 - The first three impingers are removed. The outside of each impinger is wiped off to remove excessive water and other debris. The impingers are weighed (stem included), and the weight recorded on a data sheet. The contents are poured directly into Container No. 1.

8.3.3 Sample Container No. 2 - Each of the first three impingers are rinsed sequentially with 30-ml acetone and then with 30-ml hexane, and the rinses put into Container No. 2. Material deposited in the probe is quantitatively recovered using 100-ml acetone and then 100-ml hexane and these rinses added to Container No. 2.

8.3.4 Silica gel container - The last impinger is removed, and the outside wiped to remove excessive water and other debris. It is weighed (stem included), and the weight recorded on the data sheet. The contents are transferred to the used silica gel can.

8.4 Sample preservation - Samples should be stored in the dark at 4°C. Storage times in excess of 4 weeks are not recommended.

9.0 Sample Preparation[1]

9.1 Extraction

9.1.1 Adsorbent tube - The entire contents of the adsorbent tube are expelled directly onto a glass wool plug in the sample holder of a Soxhlet extractor. Although no extraction thimble is required, a glass thimble with a coarse-fritted bottom may be used.

The tube is rinsed with 5-ml acetone and then with 15-ml hexane and these rinses put into the extractor. The extraction apparatus is assembled and the adsorbent extracted with 170-ml hexane for at least 4 hr. The extractor should cycle 10 to 14 times per hour. After allowing the extraction apparatus to cool to ambient temperature, the extract is transferred into a Kuderna-Danish evaporator.

The extract is evaporated to about 5 ml on a steam bath and the evaporator allowed to cool to ambient temperature before disassembly. The extract is transferred to a 50-ml separatory funnel and the funnel set aside.

9.1.2 Sample Container No. 1 - The aqueous sample is transferred to a 1,000-ml separatory funnel. The container is rinsed with 20-ml acetone and then with two 20-ml portions of hexane, adding the rinses to the separatory funnel.

The sample is extracted with three 100 ml portions of hexane and the sequential extracts transferred to a Kuderna-Danish evaporator.

The extract is concentrated to about 5 ml and allowed to cool to ambient temperature before disassembly. The extract is filtered through a micro column of anhydrous sodium sulfate into a 50-ml separatory funnel containing the corresponding Florisil extract from Section 9.1.1. The micro column is prepared by placing a small plug of glass wool in the bottom of the large portion of a disposable pipette and then adding anhydrous sodium sulfate until the tube is about half full.

9.1.3 Sample Container No. 2 - The organic solution is transferred into a 1,000-ml separatory funnel. The container is rinsed with two 20 ml portions of hexane and the rinses added to the separatory funnel. The sample is washed with three 100 ml portions of water. The aqueous layer is discarded and the organic layer transferred to a Kuderna-Danish evaporator.

The extract is concentrated to about 5 ml and allowed to cool to ambient temperature before disassembly. The extract is filtered through a micro column of anhydrous sodium sulfate into the 50-ml separatory funnel containing the corresponding Florisil and impinger extracts (Section 9.1.2).

9.2 Cleanup - Two tested cleanup techniques are described below.[4] Depending upon the complexity of the sample, one or both of the techniques may be required to fractionate the PCBs from interferences. If the sample extract is colored, the Florisil column cleanup may be indicated.

9.2.1 Acid cleanup

9.2.1.1 Add 5 ml of concentrated sulfuric acid to the separatory funnel containing the sample extract and shake for 1 min.

9.2.1.2 Allow the phases to separate, transfer the sample (upper phase) with three 1 to 2 ml solvent rinses to Kuderna-Danish evaporator and concentrate to an appropriate volume.

9.2.1.3 Analyze as described in Section 10.0.

9.2.1.4 If the sample is highly contaminated, a second or third acid cleanup may be employed.

9.2.2 Florisil column cleanup

9.2.2.1 Variations among batches of Florisil may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of Florisil can then be adjusted accordingly.

9.2.2.2 Place a 20-g charge of Florisil, activated overnight at 130°C, into a Chromaflex column. Settle the Florisil by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the Florisil. Pre-elute the column with 70-80 ml of hexane. Just before the exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

9.2.2.3 Add the sample extract to the column. Add 225 ml of hexane to the column. Carefully wash down the inner wall of the column with a small amount of the hexane prior to adding the total volume. Discard the first 25 ml.

9.2.2.4 Collect 200 ml of hexane eluate in a Kuderna-Danish flask. All of the PCBs should be in this fraction. Concentrate to an appropriate volume.

9.2.2.5 Analyze the sample as described in Section 10.0.

10.0 Gas Chromatographic/Electron Impact Mass Spectrometric Determination

10.1 Internal standard addition - Pipet an appropriate volume of internal standard solution SSxxx into the sample. The final concentration of the internal standards must be in the working range of the calibration and well above the matrix background. The internal standards are thoroughly mixed by mechanical agitation.

Note: The volume measurement of the spiking solution is critical to the overall method precision. The analyst must exercise caution that the volume is known ±1% or better. Where necessary, calibration of the pipet is recommended.

Note: This same solution is used as a surrogate standard solution in the protocols for products/product waste and for water. In this protocol, the ^{13}C-labeled PCBs are spiked after extraction, so are used as internal standards.

Alternately, another internal standard solution such as the d_6-3,3',4,4'-tetrachlorobiphenyl used in the product/product waste and water protocols may be used, if acceptable RF precision and accuracy are shown across the homolog range.

10.2 Tables 2, and 5 through 8 summarize the recommended operating conditions for analysis. Figure 5 presents an example of a chromatogram.

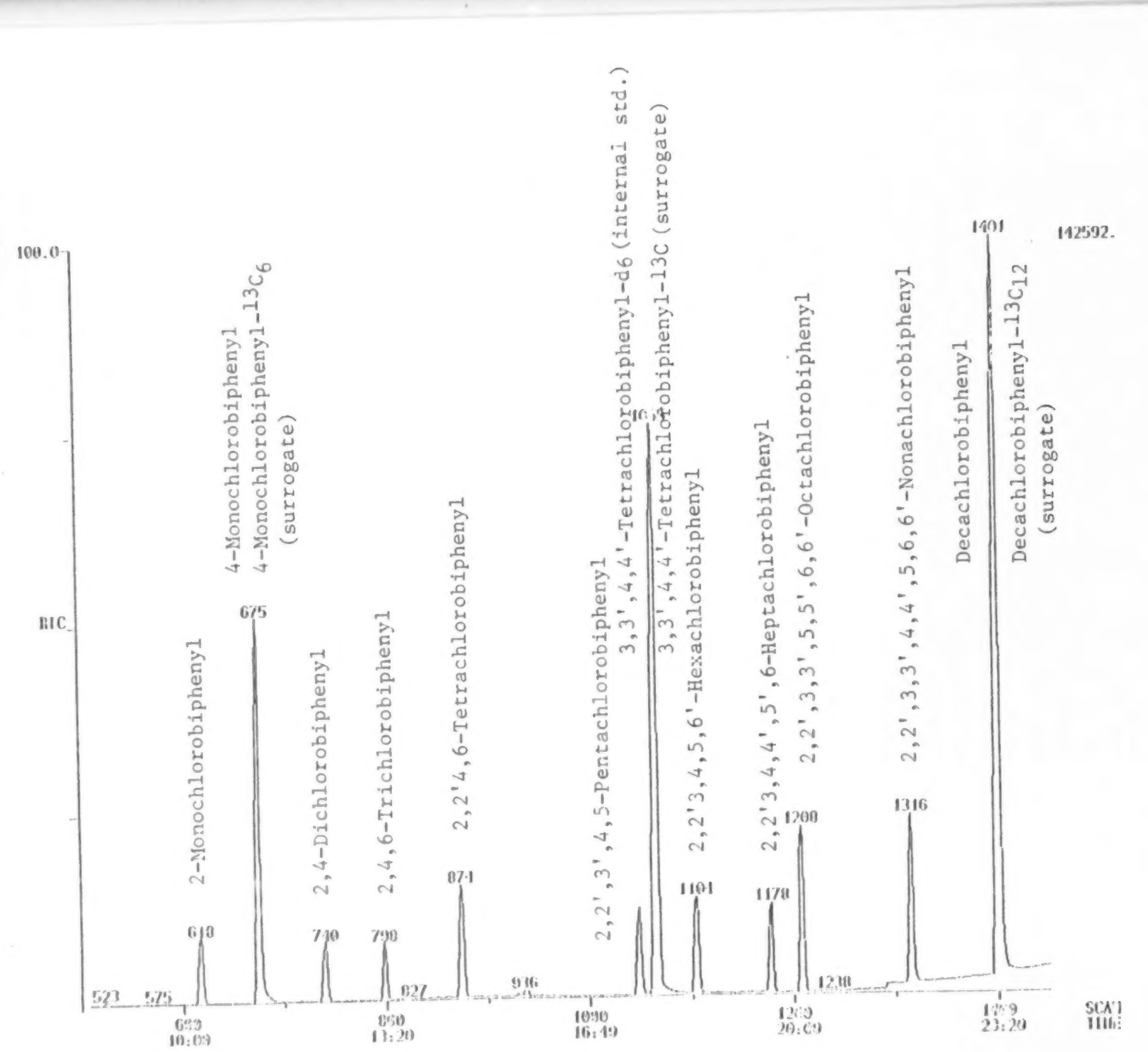

Figure 5. Capillary gas chromatography/electron impact ionization mass spectrometry (CGC/EIMS) chromatogram or the calibration standard solution required for quantitation of PCBs by homolog. This chromatogram includes PCBs representative of each homolog, three carbon-13 labeled surrogates, and the deuterated internal standard. The concentration of all components and the CGC/EIMS parameters are presented in Tables 3, 4, 5, and 7.

10.3 While the highest available chromatographic resolution is not a necessary objective of this protocol, good chromatographic performance is recommended. With the high resolution of CGC, the probability that the chromatographic peaks consist of single compounds is higher than with PGC. Thus, qualitative and quantitative data reduction should be more reliable.

10.4 After performance of the system has been certified for the day and all instrument conditions set according to Tables 2, and 5 through 8, inject an aliquot of the sample onto the GC column. If the response for any ion, including surrogates and internal standard, exceeds the working range of the system, dilute the sample and reanalyze. If the responses of surrogates, internal standard, or analytes are below the working range, recheck the system performance. If necessary, concentrate the sample and reanalyze.

10.5 Record all data on a digital storage device (magnetic disk, tape, etc.) for qualitative and quantitative data reduction as discussed below.

11.0 Qualitative Identification

11.1 Selected ion monitoring (SIM) or limited mass scan (LMS) data - The identification of a compound as a given PCB homolog requires that two criteria be met:

11.1.1 (1) The peak must elute within the retention time window set for that homolog (Section 7.6); and (2) the ratio of two ions obtained by SIM (Table 11) or by LMS (Table 12) must match the natural ratio within ±20%. The analyst must search the higher mass windows, in particular M+70, to prevent misidentification of a PCB fragment ion cluster as the parent.

11.1.2 If one or the other of these criteria is not met, interferences may have affected the results and a reanalysis using full scan EIMS conditions is recommended.

11.2 Full scan data

11.2.1 The peak must elute within the retention time windows set for that homolog (as described in Section 7.6).

11.2.2 The unknown spectrum must match that of an authentic PCB. The intensity of the three largest ions in the molecular cluster (two largest for monochlorobiphenyls) must match the natural ratio within ±20%. Frequent clusters with proper intensity ratios must also be present.

11.2.3 Alternatively, a spectral search may be used to automatically reduce the data. The criteria for acceptable

TABLE 11. CHARACTERISTIC SIM IONS FOR PCBs

Homolog	Ion (relative intensity) Primary	Secondary	Tertiary
$C_{12}H_9Cl$	188 (100)	190 (33)	-
$C_{12}H_8Cl_2$	222 (100)	224 (66)	226 (11)
$C_{12}H_7Cl_3$	256 (100)	258 (99)	260 (33)
$C_{12}H_6Cl_4$	292 (100)	290 (76)	294 (49)
$C_{12}H_5Cl_5$	326 (100)	328 (66)	324 (61)
$C_{12}H_4Cl_6$	360 (100)	362 (82)	364 (36)
$C_{12}H_3Cl_7$	394 (100)	396 (98)	398 (54)
$C_{12}H_2Cl_8$	430 (100)	432 (66)	428 (87)
$C_{12}HCl_9$	464 (100)	466 (76)	462 (76)
$C_{12}Cl_{10}$	498 (100)	500 (87)	496 (68)

Source: Rote, J. W., and W. J. Morris, "Use of Isotopic Abundance Ratios in Identification of Polychlorinated Biphenyls by Mass Spectrometry," J. Assoc. Offic. Anal. Chem., 56(1), 188-199 (1973).

TABLE 12. LIMITED MASS SCANNING (LMS) RANGES FOR PCBs

Compound	Mass range (m/z)[a]
$C_{12}H_9Cl_1$	186-190
$C_{12}H_8Cl_2$	220-226
$C_{12}H_7Cl_3$	254-260
$C_{12}H_6Cl_3$	288-294
$C_{12}H_5Cl_5$	322-328
$C_{12}H_4Cl_6$	356-364
$C_{12}H_3Cl_7$	386-400
$C_{12}H_2Cl_8$	426-434
$C_{12}HCl_9$	460-468
$C_{12}Cl_{10}$	494-504
$C_{12}D_6Cl_4$	294-300
$^{13}C_6{}^{12}C_6H_9Cl$	192-196
$^{13}C_{12}H_6Cl_4$	300-306
$^{13}C_{12}H_2Cl_8$	438-446
$^{13}C_{12}Cl_{10}$	506-516

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[a] Adapted from Tindall, G. W., and P. E. Wininger, "Gas Chromatography-Mass Spectrometry Method for Identifying and Determining Polychlorinated Biphenyls," J. Chromatogr., 196, 109-119 (1980).

identification include a high index of similarity. For the Incos 2300, a fit of 750 or greater must be obtained.

11.3 Disputes in interpretation - Where there is reasonable doubt as to the identity of a peak as a PCB, the analyst must either identify the peak as a PCB or proceed to a confirmational analysis (see Section 13.0).

12.0 Quantitative Data Reduction

12.1 Once a chromatographic peak has been identified as a PCB, the compound is quantitated based either on the integrated abundance of the SIM data or EICP for the primary characteristic ion in Tables 11 and 12. If interferences are observed for the primary ion, use the secondary and then tertiary ion for quantitation. If interferences in the parent cluster prevent quantitation, an ion from a fragment cluster (e.g., M-70) may be used. Whichever ion is used, the RF must be determined using that ion. The same criteria should be applied to the internal standard compounds (Table 13).

12.2 Using the appropriate response factor (RF_p) as determined in Section 7.3, calculate the mass of each PCB peak (M_p) using Equation 12-1.

$$M_p = \frac{A_p}{A_{is}} \cdot \frac{1}{RF_p} \cdot M_{is} \qquad \text{Eq. 12-1}$$

where A_p = area of the characteristic ion for the analyte PCB peak

A_{is} = area of the characteristic ion for the internal standard peak

RF_p = response factor of a given PCB congener

M_{is} = mass of internal standard injected (micrograms)

12.3 If a peak appears to contain non-PCB interferences which cannot be circumvented by a secondary or tertiary ion, either:

12.3.1 Reanalyze the sample on a different column which separates the PCB and interferents;

12.3.2 Perform additional chemical cleanup (Section 9) and then reanalyze the sample; or

12.3.3 Quantitate the entire peak as PCB.

12.4 Sum all of the peaks for each homolog and then sum those to yield the total PCB mass, M_T, in the sample. If a concentration-per-peak or concentration-per-homolog reporting format is desired, carry each value through the calculations in an appropriate manner.

TABLE 13. CHARACTERISTIC IONS FOR ^{13}C-LABELED PCB SURROGATES

Specific compound	Ion (relative intensity)		
	Primary	Secondary	Tertiary
$^{13}C_6{}^{12}C_6H_9Cl$	194 (100)	196 (33)	-
$^{13}C_{12}H_6Cl_4$	304 (100)	306 (49)	302 (78)
$^{13}C_{12}H_2Cl_8$	442 (100)	444 (65)	440 (89)
$^{13}C_{12}Cl_{10}$	510 (100)	512 (87)	514 (50)

12.5 Calculation of air sample volume[1]

12.5.1 Nomenclature

M_p = Mass of PCB represented by a chromatographic peak micrograms

M_T = Total mass of PCBs in sample, micrograms

C_a = Concentration of PCBs in air, micrograms per cubic meter, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis

A_n = Cross-sectional area of nozzle, square meter (square feet)

B_{ws} = Water vapor in the gas stream, proportion by volume

I = Percent of isokinetic sampling

MW_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole)

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg)

P_s = Absolute stack gas pressure, mm Hg (in. Hg)

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in Hg)

R = Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.83 in. Hg-ft^3/°R-lb-mole)

T_m = Absolute average dry gas meter temperature °K (°R)

T_s = Absolute average stack gas temperature °K (°R)

T_{std} = Standard absolute temperature, 293°K (528°R)

V_{1c} = Total volume of liquid collected in impingers and silica gel, milliliters. Volume of water collected equals the weight increase in grams times 1 ml/g

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf)

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf)

$V_{w(std)}$ = Volume of water vapor in the gas sample corrected to standard conditions, scm (scf)

V_t = Total volume of sample, milliliter

V_s = Stack gas velocity, calculated by EPA Method 2, m/sec (ft/sec)

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O)

ρ_w = Density of water, 1 g/ml (0.00220 lb/ml)

θ = Total sampling time, minutes

13.6 = Specific gravity of mercury

60 = Seconds per minute

100 = Conversion to percent

12.5.2 Average dry gas meter temperature and average orifice pressure drop - See data sheet (Figure 4).

12.5.3 Dry gas volume - Correct the sample volume measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68°F, 29.92 in. Hg)] by using Equation 12-2.

$$V_{m(std)} = V_m \frac{T_{std}}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} = K\, V_m \frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m} \qquad \text{Eq. 12-2}$$

where K = 0.3855°K/mm Hg for metric units
= 17.65 °R/in. Hg for English units

12.5.4 Volume of water vapor

$$V_{w(std)} = V_{1c} \frac{\rho_w}{MW_w} \frac{RT_{std}}{P_{std}} = K\, V_{1c} \qquad \text{Eq. 12-3}$$

where K = 0.00134 m^3/ml for metric units
= 0.0472 ft^3/ml for English units

12.5.5 Moisture content

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 12-4}$$

If the liquid droplets are present in the gas stream, assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

12.6 Concentration of PCBs in stack gas - Determine the concentration of PCBs in the air according to Equation 12-5 and report in micrograms per cubic meter using Table 14. If an alternate reporting format (e.g., concentration per peak) is desired, a different report form may be used.

$$C_a = K \frac{M_T}{V_{m(std)}} \qquad \text{Eq. 12-5}$$

where $K = 35.31\ \text{ft}^3/\text{m}^3$

12.7 Isokinetic variation

12.7.1 Calculations from raw data.

$$I = \frac{100\ T_s\ [K\ V_{1c} + (V_m/T_m)\ (P_{bar}) + \Delta H/13.6)]}{60\ \theta\ V_s\ P_s\ A_n} \qquad \text{Eq. 12-6}$$

where K = 0.00346 mm $\text{Hg-m}^3/\text{ml-°K}$ for metric units
= 0.00267 in. $\text{Hg-ft}^3/\text{ml-°R}$ for English units

12.7.2 Calculations from intermediate values

$$I = \frac{T_s\ V_{m(std)}\ P_{std}\ 100}{T_{std}\ V_s\ \theta\ A_n\ P_s\ 60\ (1-B_{ws})} \qquad \text{Eq. 12-7}$$

$$= K \frac{T_s\ V_{m(std)}}{P_s\ V_s\ A_n\ \theta\ (1-B_{ws})}$$

where K = 4.323 for metric units
= 0.0944 for English units

12.7.3 Acceptable results - The following range sets the limit on acceptable isokinetic sampling results:

If $90\% < I < 110\%$, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Agency may opt to accept the results.

12.8 Round off all numbers reported to two significant figures.

13.0 Confirmation

If there is reason to question the qualitative identification (Section 11.0), the analyst may choose to confirm that a peak is not a PCB. Any technique may be chosen provided that it is validated as having equivalent or superior selectivity and sensitivity to GC/EIMS. Some candidate techniques include alternate GC columns (with EIMS detection), GC/CIMS, GC/NCIMS, high resolution EIMS, and MS/MS techniques. Each laboratory

TABLE 14. ANALYSIS REPORT

INCIDENTAL PCBs IN AIR

Sample No. ______________________
Sample Matrix ____________________
Sample Source ____________________
Notebook No. or File Location _______

Volume Collected [$V_{m(std)}$] ____________ m^3
Mass of Internal Standard Injected, M_{is} _____________ µg

			Qualitative					Quantitative		
Analyte	1°	2°	$I_{1°}$	$I_{2°}$	Ratio	Theoretical	OK?	Ion Used	RF	Mass M_p (µg)
IS	298	246				100/76			1.000	
1-Cl	188	190				100/33				
2-Cl	222	224				100/66				
3-Cl	256	258				100/99				
4-Cl	292	290				100/76				
5-Cl	326	328				100/66				
6-Cl	360	362				100/82				
7-Cl	394	396				100/98				
8-Cl	430	432				100/66				
9-Cl	464	466				100/76				
10-Cl	498	500				100/87				

Total (M_T) __________ µg
Concentration (C_A) __________ µg/m^3

Reported by:	Internal Audit:	EPA Audit:
Name	Name	Name
Signature/Date	Signature/Date	Signature/Date
Organization	Organization	Organization

must validate confirmation techniques to show equivalent or superior selectivity between PCBs and interferences and sensitivity (limit of quantitation, LOQ).

If a peak is confirmed as being a non-PCB, it may be deleted from the calculation (Section 12). If a peak is confirmed as containing both PCB and non-PCB components, it must be quantitated according to Section 12.3.

14.0 Quality Control

14.1 Each laboratory that uses this method must operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory must maintain performance records to define the quality of data that are generated. After a date specified by the Agency, ongoing performance checks should be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

14.2 The analysts must certify that the precision and accuracy of the analytical results are acceptable by:

14.2.1 The absolute precision of surrogate recovery, measured as the RSD_s of the integrated EIMS area (A_s) for a set of samples, must be ±10%.

14.2.2 The mean recovery (R_c) of at least four replicates of a QC check sample to be supplied by the Agency must meet Agency-specified accuracy and precision criteria. This forms the initial data base for establishing control limits (see Section 14.3 below).

14.3 Control limits - The laboratory must establish control limits using the following equations:

Upper control limit (UCL) = $R_c + 3\ RSD_c$

Upper warning limit (UWL) = $R_c + 2\ RSD_c$

Lower warning limit (LWL) = $R_c - 2\ RSD_c$

Lower control limit (LCL) = $R_c - 3\ RSD_c$

These may be plotted on control charts. If an analysis of a check sample falls outside the warning limits, the analyst should be alerted that potential problems may need correction. If the results for a check sample fall outside the control limits, the laboratory must take corrective action and recertify the performance

(Section 14.2) before proceeding with analyses. The warning and control limits should be continuously updated as more check sample replicates are added to the data base.

14.4 Before processing any samples, the analyst should demonstrate through the analysis of a reagent blank that all glassware and reagent interferences are under control. Each time a set of samples is analyzed or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against contamination.

14.5 Procedural QC - The various steps of the analytical procedure should have quality control measures. These include but are not limited to:

14.5.1 GC performance - See Section 7.1 for performance criteria.

14.5.2 MS performance - See Section 7.2 for performance criteria.

14.5.3 Qualitative identification - At least 10% of the PCB identifications, as well as any questionable results, should be confirmed by a second mass spectrometrist.

14.5.4 Quantitation - At least 10% of all manual calculations, including peak area calculation, must be checked. After changes in computer quantitation routes, the results should be manually checked.

14.6 A minimum of 10% of all samples, one sample per month or one sample per matrix type, whichever is greater, must be selected at random, sampled, and analyzed in triplicate to monitor the precision of the analysis. An RSD of ±30% or less must be achieved. If the precision is greater than ±30%, the analyst must be recertified (see Section 14.2).

14.7 A minimum of 10% of all samples, one sample per month or one sample per matrix type, whichever is greater, selected at random, must be analyzed by the standard addition technique. Two aliquots of the sample are analyzed, one "as is" and one spiked with a sufficient amount of solution CSxxx to yield approximately 100 µg/sample of each compound. The spiking compounds are thoroughly incorporated by mechanical agitation. For the liquid impinger contents, shaking for 30 sec should be sufficient. For the Florisil, 10 min tumbling is recommended. For filters where inadequate incorporation may be expected, overnight equilibration with agitation is recommended.

Note: The volume measurement of the spiking solution is critical to the overall method precision. The analyst must exercise caution that the volume is known to ±1% or better. Where necessary, calibration of the pipet is recommended.

The samples are analyzed together and the quantitative results calculated. The recovery of the spiked compounds (calculated by difference) must be 80-120%. If the sample is known to contain specific PCB isomers, these isomers may be substituted for solution CSxxx. If the concentrations of PCBs are known to be high, the amount added should be adjusted so that the spiking level is 1.5 to 4 times the measured PCB level in the unspiked sample.

14.8 Sampling efficiency - The efficiency of PCB collection during sampling should be monitored. This may be achieved by adding a known amount of the ^{13}C surrogate spiking solution (Section 6.4) sufficient to give an analytical signal well above background to the first impinger prior to sampling. The recovery of the four compounds should be > 80%.

14.9 Interlaboratory comparison - Interlaboratory comparison studies are planned. Participation requirements, level of performance, and the identity of the coordinating laboratory will be presented in later revisions.

14.10 It is recommended that the participating laboratory adopt additional QC practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates or triplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

15.0 Quality Assurance

Each participating laboratory must develop a quality assurance plan according to EPA guidelines.[5] The quality assurance plan must be submitted to the Agency for approval.

16.0 Method Performance

The method performance is being evaluated. Limits of quantitation; average intralaboratory recoveries, precision, and accuracy; and interlaboratory recoveries, precision, and accuracy will be presented.

17.0 Documentation and Records

Each laboratory is responsible for maintaining full records of the analysis. Laboratory notebooks should be used for handwritten records. GC/MS data must be archived on magnetic tape, disk, or a similar device. Hard copy printouts may be kept in addition if desired. QC records should be maintained separately from sample analysis records.

The documentation must describe completely how the analysis was performed. Any variances from the protocol must be noted and fully described. Where the protocol lists options (e.g., sample cleanup), the option used and specifies (solvent volumes, digestion times, etc.) must be stated.

REFERENCES

1. Haile, C. L., and E. Baladi, "Methods for Determining the Polychlorinated Biphenyl Emissions from Incineration and Capacitor and Transformer Filling Plants," U.S. Environmental Protection Agency, (1977) EPA-600/4-73-048.

2. U.S. Environmental Protection Agency, Federal Register, 42(160), Thursday, August 18, 1977.

3. Martin, R. M., "Construction Details of Isokinetic Source Sampling Equipment," Environmental Protection Agency, Air Pollution Control Office Publication No. APTD-0581.

4. Bellar, T. A., and J. J. Lichtenberg, "The Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils," Prepared for U.S. Environmental Protection Agency, (1981) EPA-600/4-81-045.

5. Quality Assurance Program Plan for the Office of Toxic Substances, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., October 1980.

APPENDIX D

ANALYTICAL METHOD: THE ANALYSIS OF BY-PRODUCT CHLORINATED BIPHENYLS IN INDUSTRIAL WASTEWATER

THE ANALYSIS OF BY-PRODUCT CHLORINATED BIPHENYLS IN INDUSTRIAL WASTEWATER

1.0 Scope and Application

1.1 This is a gas chromatographic/electron impact mass spectrometric (GC/EIMS) method applicable to the determination of chlorinated biphenyls (PCBs) in industrial wastewater. The PCBs present may originate either as synthetic by-products or as contaminants derived from commercial PCB products (e.g., Aroclors). The PCBs may be present as single isomers or complex mixtures and may include all 209 congeners from monochlorobiphenyl through decachlorobiphenyl listed in Table 1.

1.2 The detection and quantitation limits are dependent upon the volume of sample extracted the complexity of the sample matrix and the ability of the analyst to remove interferents and properly maintain the analytical system. The method accuracy and precision will be determined in future studies.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography/mass spectrometry (GC/MS) and in the interpretation of gas chromatograms and mass spectra. Prior to sample analysis, each analyst must demonstrate the ability to generate acceptable results with this method by following the procedures described in Section 14.2.

1.4 The validity of the results depends on equivalent recovery of the analyte and ^{13}C PCBs. If the ^{13}C PCBs are not thoroughly incorporated in the matrix, the method is not applicable.

1.5 During the development and testing of this method, certain analytical parameters and equipment designs were found to affect the validity of the analytical results. Proper use of the method requires that such parameters or designs must be used as specified. These items are identified in the text by the word "must." Anyone wishing to deviate from the method in areas so identified must demonstrate that the deviation does not affect the validity of the data. Alternative test procedure approval must be obtained from the Agency. An experienced analyst may make modifications to parameters or equipment identified by the term "recommended." Each time such modifications are made to the method, the analyst must repeat the procedure in Section 14.2. In this case, formal approval is not required, but the documented data from Section 14.2 must be on file as part of the overall quality assurance program.

TABLE 1. NUMBERING OF PCB CONGENERS[a]

No.	Structure
	Monochlorobiphenyls
1	2
2	3
3	4
	Dichlorobiphenyls
4	2,2'
5	2,3
6	2,3'
7	2,4
8	2,4'
9	2,5
10	2,6
11	3,3'
12	3,4
13	3,4'
14	3,5
15	4,4'
	Trichlorobiphenyls
16	2,2',3
17	2,2',4
18	2,2',5
19	2,2',6
20	2,3,3'
21	2,3,4
22	2,3,4'
23	2,3,5
24	2,3,6
25	2,3',4
26	2,3',5
27	2,3',6
28	2,4,4'
29	2,4,5
30	2,4,6
31	2,4',5
32	2,4',5
33	2',3,4
34	2',3,5
35	3,3',4
36	3,3',5
37	3,4,4'
38	3,4,5
39	3,4',5
	Tetrachlorobiphenyls
40	2,2',3,3'
41	2,2',3,4
42	2,2',3,4'
43	2,2',3,5
44	2,2',3,5'
45	2,2',3,6
46	2,2',3,6'
47	2,2',4,4'
48	2,2',4,5
49	2,2',4,5'
50	2,2',4,6
51	2,2',4,6'
	Tetrachlorobiphenyls
52	2,2',5,5'
53	2,2',5,6'
54	2,2',6,6'
55	2,3,3',4
56	2,3,3',4'
57	2,3,3',5
58	2,3,3',5'
59	2,3,3',6
60	2,3,4,4'
61	2,3,4,5
62	2,3,4,6
63	2,3,4',5
64	2,3,4',6
65	2,3,5,6
66	2,3',4,4'
67	2,3',4,5
68	2,3',4,5'
69	2,3',4,6
70	2,3',4',5
71	2,3',4',6
72	2,3',5,5'
73	2,3',5',6
74	2,4,4',5
75	2,4,4',6
76	2',3,4,5
77	3,3',4,4'
78	3,3',4,5
79	3,3',4,5'
80	3,3',5,5'
81	3,4,4',5
	Pentachlorobiphenyls
82	2,2',3,3',4
83	2,2',3,3',5
84	2,2',3,3',6
85	2,2',3,4,4'
86	2,2',3,4,5
87	2,2',3,4,5'
88	2,2',3,4,6
89	2,2',3,4,6'
90	2,2',3,4',5
91	2,2',3,4',6
92	2,2',3,5,5'
93	2,2',3,5,6
94	2,2',3,5,6'
95	2,2',3,5',6
96	2,2',3,6,6'
97	2,2',3',4,5
98	2,2',3',4,6
99	2,2',4,4',5
100	2,2',4,4',6
101	2,2',4,5,5'
102	2,2',4,5,6'
103	2,2',4,5',6
104	2,2',4,6,6'
	Pentachlorobiphenyls
105	2,3,3',4,4'
106	2,3,3',4,5
107	2,3,3',4',5
108	2,3,3',4,5'
109	2,3,3',4,6
110	2,3,3',4',6
111	2,3,3',5,5'
112	2,3,3',5,6
113	2,3,3',5',6
114	2,3,4,4',5
115	2,3,4,4',6
116	2,3,4,5,6
117	2,3,4',5,6
118	2,3',4,4',5
119	2,3',4,4',6
120	2,3',4,5,5'
121	2,3',4,5',6
122	2',3,3',4,5
123	2',3,4,4',5
124	2',3,4,5,5'
125	2',3,4,5,6'
126	3,3',4,4',5
127	3,3',4,5,5'
	Hexachlorobiphenyls
128	2,2',3,3',4,4'
129	2,2',3,3',4,5
130	2,2',3,3',4,5'
131	2,2',3,3',4,6
132	2,2',3,3',4,6'
133	2,2',3,3',5,5'
134	2,2',3,3',5,6
135	2,2',3,3',5,6'
136	2,2',3,3',6,6'
137	2,2',3,4,4',5
138	2,2',3,4,4',5'
139	2,2',3,4,4',6
140	2,2',3,4,4',6'
141	2,2',3,4,5,5'
142	2,2',3,4,5,6
143	2,2',3,4,5,6'
144	2,2',3,4,5',6
145	2,2',3,4,6,6'
146	2,2',3,4',5,5'
147	2,2',3,4',5,6
148	2,2',3,4',5,6'
149	2,2',3,4',5',6
150	2,2',3,4',6,6'
151	2,2',3,5,5',6
152	2,2',3,5,6,6'
153	2,2',4,4',5,5'
154	2,2',4,4',5,6'
155	2,2',4,4',6,6'
156	2,3,3',4,4',5
157	2,3,3',4,4',5'
158	2,3,3',4,4',6
159	2,3,3',4,5,5'
160	2,3,3',4,5,6
	Hexachlorobiphenyls
161	2,3,3',4,5',6
162	2,3,3',4',5,5'
163	2,3,3',4',5,6
164	2,3,3',4',5',6
165	2,3,3',5,5',6
166	2,3,4,4',5,6
167	2,3',4,4',5,5'
168	2,3',4,4',5',6
169	3,3',4,4',5,5'
	Heptachlorobiphenyls
170	2,2',3,3',4,4',5
171	2,2',3,3',4,4',6
172	2,2',3,3',4,5,5'
173	2,2',3,3',4,5,6
174	2,2',3,3',4,5,6'
175	2,2',3,3',4,5',6
176	2,2',3,3',4,6,6'
177	2,2',3,3',4',5,6
178	2,2',3,3',5,5',6
179	2,2',3,3',5,6,6'
180	2,2',3,4,4',5,5'
181	2,2',3,4,4',5,6
182	2,2',3,4,4',5,6'
183	2,2',3,4,4',5',6
184	2,2',3,4,4',6,6'
185	2,2',3,4,5,5',6
186	2,2',3,4,5,6,6'
187	2,2',3,4',5,5',6
188	2,2',3,4',5,6,6'
189	2,3,3',4,4',5,5'
190	2,3,3',4,4',5,6
191	2,3,3',4,4',5',6
192	2,3,3',4,5,5',6
193	2,3,3',4',5,5',6
	Octachlorobiphenyls
194	2,2',3,3',4,4',5,5'
195	2,2',3,3',4,4',5,6
196	2,2',3,3',4,4',5,6'
197	2,2',3,3',4,4',6,6'
198	2,2',3,3',4,5,5',6
199	2,2',3,3',4,5,6,6'
200	2,2',3,3',4,5',6,6'
201	2,2',3,3',4,5,5',6'
202	2,2',3,3',5,5',6,6'
203	2,2',3,4,4',5,5',6
204	2,2',3,4,4',5,6,6'
205	2,3,3',4,4',5,5',6
	Nonachlorobiphenyls
206	2,2',3,3',4,4',5,5',6
207	2,2',3,3',4,4',5,6,6'
208	2,2',3,3',4,5,5',6,6'
	Decachlorobiphenyl
209	2,2',3,3'4,4',5,5',6,6'

[a] Adapted from Ballschmiter, K. and Zell, M., Fresenius Z. Anal. Chem., 302, 20-31 (1980).

2.0 Summary

2.1 The wastewater must be sampled such that the specimen collected for analysis is representative of the whole. Statistically designed selection of the sampling position (valve, port, outfall, etc.) or time should be employed. The sample must be preserved to prevent PCB loss prior to analysis. Storage at 4°C with optional preservation at low pH is recommended.

2.2 The sample is mechanically homogenized and subsampled if necessary. The sample is then spiked with four ^{13}C PCB surrogates and the surrogates incorporated by further mechanical agitation.

2.3 The surrogate-spiked sample is extracted and cleaned up at the discretion of the analyst. Possible extraction techniques include liquid-liquid partition and sorption onto resin columns followed by solvent elution. Cleanup techniques may include liquid-liquid partition, sulfuric acid cleanup, saponification, adsorption chromatography, gel permeation chromatography or a combination of cleanup techniques. The sample is diluted or concentrated to a final known volume for instrumental determination. The EPA Method 608[1] and 625[2] extraction and cleanup procedures may be used.

2.4 The PCB content of the sample extract is determined by capillary (preferred) or packed column gas chromatography/electron impact mass spectrometry (CGC/EIMS or PGC/EIMS) operated in the selected ion monitoring (SIM), full scan, or limited mass scan (LMS) mode.

2.5 PCBs are identified by comparison of their retention time and mass spectral intensity ratios to those in calibration standards.

2.6 PCBs are quantitated against the response factors for a mixture of 11 PCB congeners, using the response of the ^{13}C surrogate to compensate for losses in workup and instrument variability.

2.7 The PCBs identified by the SIM technique may be confirmed by full scan CGC/EIMS, retention on alternate GC columns, other mass spectrometric techniques, infrared spectrometry, or other techniques, provided that the sensitivity and selectivity of the technique is demonstrated to be comparable or superior to GC/EIMS.

2.8 The analysis time is dependent on the extent of workup employed. The time required for instrumental analysis, excluding data reduction and reporting, is about 30 to 45 min.

2.9 Appropriate quality control (QC) procedures are included to assess the performance of the analyst and estimate the quality of the results. These QC procedures include the demonstration of laboratory capability: periodic analyst certification, the use of control charts, and the analysis of blanks, replicates, and standard addition samples. A quality assurance (QA) plan must be developed for each laboratory.

2.10 While several options are available throughout this method, the recommended procedure to be followed is:

2.10.1 The sample is collected according to a scheme which permits extrapolation of the sample data to the body or containers of water being sampled.

2.10.2 The sample is preserved at low pH and at 4°C to prevent any loss of PCBs or changes in matrix which may adversely affect recovery.

2.10.3 The sample is mechanically homogenized and subsampled if necessary.

2.10.4 The sample is spiked with four ^{13}C-PCB surrogates (4-chlorobiphenyl; 3,3',4,4'-tetrachlorobiphenyl; 2,2',3,3',5,5',6,6'-octachlorobiphenyl; and decachlorobiphenyl).

2.10.5 The sample is extracted.

2.10.6 The extract is cleaned up and concentrated to an appropriate volume.

2.10.7 An aliquot of the extract is analyzed by CGC/EIMS operated in the SIM mode. On-column injections onto a 15-m DB-5 capillary column, programmed (for toluene solutions) from 110° to 325°C at 10°/min after a 2 min hold is used. Helium at 45-cm/sec linear velocity is used as the carrier gas.

2.10.8 PCBs are identified by retention time and mass spectral intensities.

2.10.9 PCBs are quantitated against the response factors for a mixture of 11 PCB congeners.

2.10.10 The total PCBs are obtained by summing the amounts for each homolog found and the concentration is reported as micrograms per liter.

3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware, leading to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences by the analysis of laboratory reagent blanks as described in Section 14.4.

3.1.1 Glassware must be scrupulously cleaned. All glassware is cleaned as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water and rinses with tap water and reagent water. The glassware should then be drained dry and heated in a muffle furnace at 400°C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After it is dry and cool, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. It is stored inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required. All solvent lots must be checked for purity prior to use.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the sources of samples.

4.0 Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

4.2 Polychlorinated biphenyls have been tentatively classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood. Personnel must wear protective equipment, including gloves and safety glasses.

Congeners highly substituted at the meta and para positions and unsubstituted at the ortho positions are reported to be the most toxic. Extreme caution should be taken when handling these compounds neat or in concentration solution. The class includes 3,3',4,4'-tetrachlorobiphenyl (both natural abundance and isotopically labeled).

4.3 Diethyl ether should be monitored regularly to determine the peroxide content. Under no circumstances should diethyl ether be used with a peroxide content in excess of 50 ppm as an explosion could result. Peroxide test strips manufactured by EM Laboratories (available from Scientific Products Company, Cat. No. P1126-8 and other suppliers) are recommended for this test. Procedures for removal of peroxides from diethyl ether are included in the instructions supplied with the peroxide test kit.

4.4 Waste disposal must be in accordance with RCRA and applicable state rules.

5.0 Apparatus and Materials

5.1 Sampling containers - Amber glass bottles, 1-liter or other appropriate volume, fitted with screw caps lined with Teflon. Cleaned foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, samples should be protected from light using foil or a light-tight outer container. The bottle must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.2 Glassware - All specifications are suggestions only. Catalog numbers are included for illustration only.

5.2.1 Volumetric flasks - Assorted sizes.

5.2.2 Pipets - Assorted sizes, Mohr delivery.

5.2.3 Micro syringes - 10.0 μl for packed column GC analysis, 1.0 μl for on-column CGC analysis.

5.2.4 Chromatographic column - Chromaflex, 400 mm long x 19 mm ID (Kontes K-420540-9011 or equivalent).

5.2.5 Gel permeation chromatograph - GPC Autoprep 1002 (Analytical Bio Chemistry Laboratories, Inc.) or equivalent.

5.2.6 Kuderna-Danish Evaporative Concentrator Apparatus

5.2.6.1 Concentrator tube - 10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper size (Ŧ19/22 joint) is used to prevent evaporation of solvent.

5.2.6.2 Evaporative flask - 500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs (Kontes K-662750-0012 or equivalent).

5.2.6.3 Snyder column - Three ball macro (Kontes K503000-0121 or equivalent).

5.3 Balance - Analytical, capable of accurately weighing 0.0001 g.

5.4 Gas chromatography/mass spectrometer system.

5.4.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using capillary columns or packed columns. Other capillary injection techniques (split, splitless, "Grob," etc.) may be used provided the performance specifications stated in Section 7.1 are met.

5.4.2 Capillary GC column - A 12-20 m long x 0.25 mm ID fused silica column with a 0.25 µm thick DB-5 bonded silicone liquid phase (J&W Scientific) is recommended. Alternate liquid phases may include OV-101, SP-2100, Apiezon L, Dexsil 300, or other liquid phases which meet the performance specifications stated in Section 7.1.

5.4.3 Packed GC column - A 180 cm x 0.2 cm ID glass column packed with 3% SP-2250 on 100/120 mesh Supelcoport or equivalent is recommended. Other liquid phases which meet the performance specifications stated in Section 7.1 may be substituted.

5.4.4 Mass spectrometer - Must be capable of scanning from 150 to 550 Daltons every 1.5 sec or less, collecting at least five spectra per chromatographic peak, utilizing a 70-eV (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of decafluorotriphenyl phosphine [DFTPP, bis(perfluorophenyl)phenyl phosphine] is injected through the GC inlet. Any GC-to-MS interface that gives acceptable calibration points at 10 ng per injection for each PCB isomer in the calibration standard and achieves all acceptable performance criteria (Section 10) may be used. Direct coupling of the fused silica column to the MS is recommended. Alternatively, GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.4.5 A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The data system must have the capability of integrating the abundances of the selected ions between specified limits and relating integrated abundances to concentrations using the calibration procedures described in this method. The computer must have software that allows

TABLE 2. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion abundance criteria
197	Less than 1% of mass 198
198	100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present, but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number to yield an extracted ion current profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

6.0 Reagents

6.1 Solvents - All solvents must be pesticide residue analysis grade. New lots should be checked for purity by concentrating an aliquot by at least as much as is used in the procedure.

6.2 Stock standard solutions - Standards of the PCB congeners listed in Table 3 are available from Ultra Scientific, Hope, Rhode Island; or Analabs, North Haven, Connecticut.

6.3 Calibration standard stock solutions - Primary dilutions of each of the individual PCBs listed in Table 3 are prepared by weighing approximately 1-10 mg of material within 1% precision. The PCB is then dissolved and diluted to 1.0 ml with hexane. Calculate the concentration in mg/ml. The primary dilutions are stored at 4°C in screw-cap vials with Teflon cap liners. The meniscus is marked on the vial wall to monitor solvent evaporation. Primary dilutions are stable indefinitely if the seals are maintained. The validity of primary and secondary dilutions must be monitored on a quarterly basis by analyzing four quality control check samples (see Section 14.2).

6.4 Working calibration standards - Working calibration standards are prepared that are similar in PCB composition and concentration to the samples by mixing and diluting the individual standard stock solutions. Example calibration solutions are shown in Table 3. The mixture is diluted to volume with pesticide residue analysis quality hexane. The concentration is calculated in ng/ml as the individual PCBs. Dilutions are stored at 4°C in narrow-mouth, screw-cap vials with Teflon cap liners. The meniscus is marked on the vial wall to monitor solvent evaporation. These secondary dilutions can be stored indefinitely if the seals are maintained. These solutions are designated "CSxxx," where the xxx is used to encode the nominal concentration in ng/ml.

6.5 Alternatively, certified stock solutions similar to those listed in Table 3 may be available from a supplier, in lieu of the procedures described in Section 6.4.

6.6 DFTPP standard - A 50-ng/μl solution of DFTPP is prepared in acetone or another appropriate solvent.

6.7 Surrogate standard stock solution - The four ^{13}C-labeled PCBs listed in Table 4 may be available from a supplier as a certified solution. This solution may be used as received or diluted further. These solutions are designated "SSxxx," where the xxx is used to encode the nominal concentration in ng/ml.

TABLE 3. CONCENTRATIONS OF CONGENERS IN PCB CALIBRATION STANDARDS (ng/ml)[a]

Homolog	Congener no.	CS1000	CS100	CS050	CS010
1	1	1,040	104	52	10
1	3	1,000	100	50	10
2	7	1,040	104	52	10
3	30	1,040	104	52	10
4	50	1,520	152	76	15
5	97	1,740	174	87	17
6	143	1,920	192	96	19
7	183	2,600	260	130	26
8	202	4,640	464	232	46
9	207	5,060	506	253	51
10	209	4,240	424	212	42
4	210 (IS)	255	255	255	255
1	211 (RS)	104	104	104	104
4	212 (RS)	257	257	257	257
8	213 (RS)	407	407	407	407
10	214 (RS)	502	502	502	502

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[a] Concentrations given as examples only.

TABLE 4. COMPOSITION OF SURROGATE SPIKING SOLUTION (SS100) CONTAINING ^{13}C-LABELED PCBs[a]

Congener no.	Compound	Concentration (µg/ml)
211	$(1',2',3',4',5',6'-^{13}C_6)$4-chlorobiphenyl	104
212	$(^{13}C_{12})$3,3',4,4'-tetrachlorobiphenyl	257
213	$(^{13}C_{12})$2,2',3,3',5,5',6,6'-octachlorobiphenyl	395
214	$(^{13}C_{12})$decachlorobiphenyl	502

[a] Concentrations given as examples only.

6.8 Internal standard solution - A solution of d_6-3,3',4,4'-tetrachlorobiphenyl is prepared at a nominal concentration of 1-10 mg/ml in hexane. The solution is further diluted to give a working standard.

6.9 Solution stability - The calibration standard, surrogate and DFTPP solutions should be checked frequently for stability. These solutions should be replaced after 6 months, or sooner if comparison with quality control check samples indicates compound degradation or concentration change.

6.10 Quality control check samples will be supplied by the Agency.

7.0 Calibration

7.1 The gas chromatograph must meet the minimum operating parameters shown in Tables 5 and 6, daily. If all of the criteria are not met, the analyst must adjust conditions and repeat the test until all criteria are met.

7.2 The mass spectrometer must meet the minimum operating parameters shown in Tables 2, 7, and 8, daily. If all criteria are not met, the analyst must retune the spectrometer and repeat the test until all conditions are met.

7.3 The PCB response factor (RF_p) must be determined using Equation 7-1 for the analyte homologs.

$$RF_p = \frac{A_p \times M_{is}}{A_{is} \times M_p} \qquad \text{Eq. 7-1}$$

where RF_p = response factor of a given PCB isomer

A_p = area of the characteristic ion for the PCB congener peak

M_p = mass of PCB congener injected (nanograms)

A_{is} = area of the characteristic ion for the internal standard peak

M_{is} = mass of internal standard injected (nanograms)

Using the same conditions as for RF_p, the surrogate response factors (RF_s) must be determined using Equation 7-2.

$$RF_s = \frac{A_s \times M_{is}}{A_{is} \times M_s} \qquad \text{Eq. 7-2}$$

where A_s = area of the characteristic ion for the surrogate peak

M_s = mass of surrogate injected (nanograms)

Other items are the same as defined in Equation 7-1.

TABLE 5. OPERATING PARAMETERS FOR CAPILLARY COLUMN GAS CHROMATOGRAPHIC SYSTEM

Parameter	Recommended	Tolerance
Gas chromatograph	Finnigan 9610	Other[a]
Column	15 m x 0.255 mm ID Fused silica	Other
Liquid phase	DB-5 (J&W)	Other nonpolar or semipolar
Liquid phase thickness	0.25 µm	< 1 µm
Carrier gas	Helium	Hydrogen
Carrier gas velocity	45 cm/sec[b]	Optimum performance
Injector	On-column (J&W)[c]	Other
Injector temperature	Optimum performance[c]	Optimum performance
Injection volume	1.0 µl[c]	Other
Initial column temperature	70°C (2 min)[d]	Other
Column temperature program	70°-325°C at 10°C/min[e]	Other
Separator	None[f]	Glass jet or other
Transfer line temperature	280°C	Optimum[g]
Tailing factor[h]	0.7-1.5	0.4-3
Peak width[i]	7-10 sec	< 15 sec

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a Substitutions permitted with any common apparatus or technique provided performance criteria are met.

b Measured by injection of air or methane at 270°C oven temperature.

c For on-column injection, manufacturer's instructions should be followed regarding injection technique.

d With on-column injection, initial temperature equals boiling point of the solvent; in this instance, hexane.

e $C_{12}Cl_{10}$ elutes at 270°C. Programming above this temperature ensures a clean column and lower background on subsequent runs.

f Fused silica columns may be routed directly into the ion source to prevent separator discrimination and losses.

g High enough to elute all PCBs, but not high enough to degrade the column if routed through the transfer line.

h Tailing factor is width of front half of peak at 10% height divided by width of back half of peak at 10% height for single PCB congeners in solution CSxxx.

i Peak width at 10% height for a single PCB congener is CSxxx.

TABLE 6. OPERATING PARAMETERS FOR PACKED COLUMN GAS CHROMATOGRAPHY SYSTEM

Parameter	Recommended	Tolerances
Gas chromatograph	Finnigan 9610	Other[a]
Column	180 cm x 0.2 cm ID glass	Other
Column packing	3% SP-2250 on 100/ 120 mesh Supelcoport	Other nonpolar or semipolar
Carrier gas	Helium	Hydrogen
Carrier gas flow rate	30 ml/min	Optimum performance
Injector	On-column	-
Injector temperature	250°C	Optimum[b]
Injection volume	1.0 μl	≦ 5 μl
Initial column temperature	150°C, 4 min	Other
Column temperature program	150°C-260° at 8°/min	Other
Separator	Glass jet	Other
Transfer line temperature	280°C	Optimum[a]
Tailing factor[c]	0.7-1.5	0.4-3
Peak width[d]	10-20 sec	< 30 sec

---

[a] Substitutions permitted if performance criteria are met.

[b] High enough to elute all PCBs.

[c] Tailing factor is width of front half of peak at 10% height divided by width of back half of peak at 10% height for single PCB congeners in solution CSxxx.

[d] Peak width at 10% height for a single PCB congener in CSxxx.

TABLE 7. OPERATING PARAMETERS FOR QUADRUPOLE MASS SPECTROMETER SYSTEM

Parameter	Recommended	Tolerance
Mass spectrometer	Finnigan 4023	Other[a]
Data system	Incos 2400	Other
Scan range	95-550	Other
Scan time	1 sec	Other[b]
Resolution	Unit	Optimum performance
Ion source temperature	280°C	200°-300°C
Electron energy[c]	70 eV	Optimum performance
Trap current	0.2 mA	Optimum performance
Multiplier voltage	-1,600 V	Optimum performance
Preamplifier sensitivity	10^{-6} A/V	Set for desired working range

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[a] Substitutions permitted if performance criteria are met.

[b] Greater than five data points over a GC peak is a minimum.

[c] Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no separator is used.

TABLE 8. OPERATING PARAMETERS FOR MAGNETIC SECTOR MASS SPECTROMETER SYSTEM

Parameter	Recommended	Tolerance
Mass spectrometer	Finnigan MAT 311A	Other[a]
Data system	Incos 2400	Other
Scan range	98-550	Other
Scan mode	Exponential	Other
Cycle time	1.2 sec	Other[b]
Resolution	1,000	> 500
Ion source temperature	280°C	250°-300°C
Electron energy[c]	70 eV	70 eV
Emission current	1-2 mA	Optimum
Filament current	Optimum	Optimum
Multiplier	-1,600 V	Optimum

[a] Substitutions permitted if performance criteria are met.

[b] Greater than five data points over a GC peak is a minimum.

[c] Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no separator is used.

If specific congeners are known to be present and if standards are available, selected RF values may be employed. For general samples, solutions CSxxx and SSxxx or a mixture (Tables 3 and 4), with a similar level of internal standard (d_6-3,3',4,4'-tetrachlorobiphenyl) added, may be used as the response factor solution. The PCB-surrogate pairs to be used in the RF calculation are listed in Table 9.

Generally, only the primary ions of both the analyte and surrogate are used to determine the RF values. If alternate ions are to be used in the quantitation, the RF must be determined using that characteristic ion.

The RF value must be determined in a manner to assure ±20% accuracy and precision. For instruments with good day-to-day precision, a running mean ($\overline{RF}$) based on seven values determined once each day may be appropriate. Other options include, but are not limited to, triplicate determinations of a single concentration spaced throughout a day or determination of the RF at three different levels to establish a working curve.

If replicate RF values differ by greater than ±10% RSD, the system performance should be monitored closely. If the RSD is greater than ±20%, the data set must be considered invalid and the RF redetermined before further analyses are done.

7.4 If the GC/EIMS system has not been demonstrated to yield a linear response or if the analyte concentrations are more than two orders of magnitude different from those in the RF solution, a calibration curve must be prepared. If the analyte and RF solution concentrations differ by more than one order of magnitude, a calibration curve should be prepared. A calibration curve should be established with triplicate determinations at three or more concentrations bracketing the analyte levels.

7.5 The relative retention time (RRT) windows for the 10 homologs and surrogates must be determined. If all congeners are not available, a mixture of available congeners or an Aroclor mixture (e.g., 1016/1254/1260) may be used to estimate the windows. The windows must be set wider than observed if all isomers are not determined. Typical RRT windows for one column are listed in Table 10. The windows may differ substantially if other GC parameters are used.

8.0 Sample Collection, Handling, and Preservation

8.1 Amber glass sample containers should have Teflon-lined screw caps. With noncorrosive samples, methylene chloride-washed aluminum foil liners may be substituted. The volume is determined by the amount of sample to be collected but will usually be 1 liter or 1 qt. The sample size is dependent on the anticipated PCB levels and difficulty of the subsequent extraction/cleanup steps.

TABLE 9. PAIRINGS OF ANALYTE, CALIBRATION, AND SURROGATE COMPOUNDS

Analyte		Calibration standard		Surrogate	
Congener[a] no.	Compound	Congener no.	Compound	Congener no.	Compound
1	2-$C_{12}H_9Cl$	1	2	211	$^{13}C_6$-4
2,3	3- and 4-$C_{12}H_9Cl$	3	4	211	$^{13}C_6$-4
4-15	$C_{12}H_8Cl_2$	7	2,4	211	$^{13}C_6$-4
16-39	$C_{12}H_7Cl_3$	30	2,4,6	212	$^{13}C_{12}$-3,3',4,4'
40-81	$C_{12}H_6Cl_4$	50	2,2',4,6	212	$^{13}C_{12}$-3,3',4,4'
82-127	$C_{12}H_5Cl_5$	97	2,2',3',4,5	212	$^{13}C_{12}$-3,3',4,4'
128-169	$C_{12}H_4Cl_6$	143	2,2',3,4,5,6'	212	$^{13}C_{12}$-3,3',4,4'
170-193	$C_{12}H_3Cl_7$	183	2,2',3',4,4',5',6	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
194-205	$C_{12}H_2Cl_8$	202	2,2',3,3',5,5',6,6'	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
206-208	$C_{12}HCl_9$	207	2,2',3,3',4,4',5,6,6'	213	$^{13}C_{12}$-2,2',3,3',5,5',6,6'
209	$C_{12}Cl_{10}$	209	$C_{12}Cl_{10}$	214	$^{13}C_{12}Cl_{10}$

[a] Ballschmiter numbering system, see Table 1.

TABLE 10. RELATIVE RETENTION TIME (RRT) RANGES OF PCB HOMOLOGS VERSUS d_6-3,3',4,4'-TETRACHLOROBIPHENYL

PCB homolog	No. of isomers measured	Observed range of RRTs[a]	Calibration solution Congener no.	 Observed RRT[a]	Projected range of RRTs[b]
Monochloro	3	0.40-0.50	1 3	0.43 0.50	0.35-0.55
Dichloro	10	0.52-0.69	7	0.58	0.35-0.80
Trichloro	9	0.62-0.79	30	0.65	0.35-1.10
Tetrachloro	16	0.72-1.01	50	0.75	0.55-1.05
Pentachloro	12	0.82-1.08	97	0.98	0.80-1.10
Hexachloro	13	0.93-1.20	143	1.05	0.90-1.25
Heptachloro	4	1.09-1.30	183	1.15	1.05-1.35
Octachloro	6	1.19-1.36	202	1.19	1.10-1.50
Nonachloro	3	1.31-1.42	207	1.33	1.25-1.50
Decachloro	1	1.44-1.45	209	1.44	1.35-1.50

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[a] The RRTs of the 77 congeners and a mixture of Aroclor 1016/1254/1260 were measured versus 3,3',4,4'-tetrachlorobiphenyl-d_6 (internal standard) using a 15-m J&W DB-5 fused silica column with a temperature program of 110°C for 2 min, then 10°C/min to 325°C, helium carrier at 45 cm/sec, and an on-column injector. A Finnigan 4023 Incos quadrupole mass spectrometer operating with a scan range of 95-550 daltons was used to detect each PCB congener.

[b] The projected relative retention windows account for overlap of eluting homologs and take into consideration differences in operating systems and lack of all possible 209 PCB congeners.

8.2 Sample bottle preparation

8.2.1 All sample bottles and caps should be washed in detergent solution, rinsed with tap water and then with distilled water. The bottles and caps are allowed to drain dry in a contaminant-free area. Then the caps are rinsed with pesticide grade hexane and allow to air dry.

8.2.2 Sample bottles are heated to 400°C for 15 to 20 min or rinsed with pesticide grade acetone or hexane and allowed to air dry.

8.2.3 The clean bottles are stored inverted or sealed until use.

8.3 Sample collection

8.3.1 The primary consideration in sample collection is that the sample collected be representative of the whole. Therefore, sampling plans or protocols for each individual producer's situation will have to be developed. The recommendations presented here describe general situations. The number of replicates and sampling frequency also must be planned prior to sampling.

8.3.2 If possible, mix the source thoroughly before collecting the sample. If mixing is impractical, the sample should be collected from a representative area of the source. If the liquid is flowing through an enclosed system, sampling through a valve should be randomly timed.

8.3.3 Fill the bottle with water, add preservative (Section 8.4), cap tightly, and shake well. To prevent the caps from working loose during storage tape the caps on with a water-insoluble tape.

8.4 Sample preservation - Samples should be stored at 4°C. Since there is a possibility of microbial degradation, addition of H_2SO_4 during collection to a $pH < 2$ is recommended. A test strip is used to monitor the pH. Storage times in excess of 4 weeks are not recommended.

If residual chlorine is present in the sample, it should be quenched with sodium thiosulfate. EPA Methods 330.4 and 330.5 may be used to measure the residual chlorine.[3] Field test kits are available for this purpose.

9.0 Sample Preparation

9.1 Sample homogenization and subsampling - The sample is homogenized by shaking, blending, or other appropriate mechanical technique, if necessary. If the density of the sample is not between 0.9

and 1.1, the density should be determined and reported. Consideration should be given to treating the sample as a product waste (see separate protocol).

Note: The precision of the mass determination at this step will be reflected in the overall method precision. Therefore, an analytical balance must be used to assure that the weight is accurate to ±1% or better.

9.2 Surrogate addition - An appropriate volume of surrogate solution SSxxx is pipetted into the sample. The final concentration of the surrogates must be in the working range of the calibration and well above the matrix background.

Note: The volume measurement of the spiking solution is critical to the overall method precision. The analyst must exercise caution that the volume is known to ±1% or better. Where necessary, calibration of the pipet is recommended.

9.3 Sample preparation (extraction/cleanup) - After addition of the surrogates, the sample is further treated at the discretion of the analyst, provided that the GC/EIMS response of the four surrogates meets the criteria listed in Section 7.0. The literature pertaining to these techniques has been reviewed.[4] Several possible techniques are presented below for guidance only. The applicability of any of these techniques to a specific sample matrix must be determined by the precision and accuracy of the ^{13}C PCB surrogate recoveries, as discussed in Section 14.2.

9.3.1 Extraction - The entire sample must be transferred to the extraction vessel with PCB-free water washing, if necessary, to transfer all solids. The container is then rinsed with the extraction solvent to recovery any PCBs adhering to the container wall. The solvent rinses are combined with the extracts from below. Measure the sample volume to the nearest 0.5%.

9.3.1.1 Liquid-liquid extraction - The solvent, number of extractions, solvent-to-sample ratio, and other parameters are chosen at the analyst's discretion. A suggested extraction from water is presented in EPA Methods 608[1] and 625.[2]

9.3.1.2 Sorbent column extraction - PCBs may be isolated from water onto sorbent columns, although these techniques are not as widely used or thoroughly validated as liquid-liquid extraction. The selection of sorbent (XAD, Porapak, carbon-polyurethane foam, etc.) will depend on the nature of the matrix. The available methods have been reviewed.[4]

9.3.2 Cleanup - Several tested cleanup techniques are described below. All but the base cleanup (9.3.2.8) were previously validated for PCBs in transformer fluids.[5] Depending upon the complexity of the sample, one or more of the techniques may be required to fractionate the PCBs from interferences. For most cleanups a concentrated (1-5 ml) extract should be used.

9.3.2.1 Acid cleanup

9.3.2.1.1 Place 5 ml of concentrated sulfuric acid into a 40-ml narrow-mouth screw-cap bottle. Add the sample extract. Seal the bottle with a Teflon-lined screw cap and shake for 1 min.

9.3.2.1.2 Allow the phases to separate, transfer the sample (upper phase) with three rinses of 1-2 ml solvent to a clean container and concentrate to an appropriate volume.

9.3.2.1.3 Analyze as described in Section 10.0.

9.3.2.1.4 If the sample is highly contaminated, a second or third acid cleanup may be employed.

9.3.2.2 Florisil column cleanup

9.3.2.2.1 Variations among batches of Florisil (PR grade or equivalent) may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of Florisil can then be adjusted accordingly.

9.3.2.2.2 Place a 20-g charge of Florisil, activated overnight at 130°C, into a Chromaflex column. Settle the Florisil by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the Florisil. Pre-elute the column with 70-80 ml of hexane. Just before the exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

9.3.2.2.3 Add the sample extract to the column.

9.3.2.2.4 Carefully wash down the inner wall of the column with 5 ml of the hexane.

9.3.2.2.5 Add 220 ml of hexane to the column.

9.3.2.2.6 Discard the first 25 ml.

9.3.2.2.7 Collect 200 ml of hexane eluate in a Kuderna-Danish flask. All of the PCBs should be in this fraction. Concentrate to an appropriate volume.

9.3.2.2.8 Analyze the sample as described in Section 10.0.

9.3.2.3 Alumina column cleanup

9.3.2.3.1 Adjust the activity of the alumina (Fisher A540 or equivalent) by heating to 200°C for 2 to 4 hr. When cool, add 3% water (wt:wt) and mix until uniform. Store in a tightly sealed bottle. Allow the deactivated alumina to equilibrate at least 1/2 hr before use. Reactivate weekly.

9.3.2.3.2 Variations between batches of alumina may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of alumina can then be adjusted accordingly.

9.3.2.3.3 Place a 50-g charge of alumina into a Chromaflex column. Settle the alumina by tapping. Add about 1 cm of anhydrous sodium sulfate. Pre-elute the column with 70-80 ml of hexane. Just before exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

9.3.2.3.4 Add the sample extract to the column.

9.3.2.3.5 Carefully wash down the inner wall of the column with 5 ml volume of hexane.

9.3.2.3.6 Add 295 ml of hexane to the column.

9.3.2.3.7 Discard the first 50 ml.

9.3.2.3.8 Collect 250 ml of the hexane in a Kuderna-Danish flask. All of the PCBs should be in this fraction. Concentrate to an appropriate volume.

9.3.2.3.9 Analyze the sample as described in Section 10.0.

9.3.2.4 Silica gel column cleanup

9.3.2.4.1 Activate silica gel (Davison grade 950 or equivalent) at 135°C overnight.

9.3.2.4.2 Variations between batches of silica gel may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of silica gel can then be adjusted accordingly.

9.3.2.4.3 Place a 25-g charge of activated silica gel into a Chromaflex column. Settle the silica gel by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the silica gel.

9.3.2.4.4 Pre-elute the column with 70-80 ml of hexane. Discard the eluate. Just before exposing the sodium sulfate layer to air, stop the flow.

9.3.2.4.5 Add the sample extract to the column.

9.3.2.4.6 Wash down the inner wall of the column witb 5 ml of hexane.

9.3.2.4.7 Elute the PCBs with 195 ml of 10% diethyl ether in hexane (v:v).

9.3.2.4.8 Collect 200 ml of the eluate in a Kuderna-Danish flask. All of the PCBs should be in this fraction. Concentrate to an appropriate volume.

9.3.2.4.9 Analyze the sample according to Section 10.0.

9.3.2.5 Gel permeation cleanup

9.3.2.5.1 Set up and calibrate the gel permeation chromatograph with an SX-3 column according to the Autoprep instruction manual. Use 15% methylene chloride in cyclohexane (v:v) as the mobile phase.

9.3.2.5.2 Inject 5.0 ml of the sample extract into the instrument. Collect the fraction containing the PCBs (see Autoprep operator's manual) in a Kuderna-Danish flask equipped with a 10-ml ampul.

9.3.2.5.3 Concentrate the PCB fraction to an appropriate volume.

9.3.2.5.4 Analyze as described in Section 10.0.

9.3.2.6 Acetonitrile partition

9.3.2.6.1 Place the sample extract into a 125-ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for 1 min with 30-ml portions of hexane-saturated acetonitrile.

9.3.2.6.2 Combine and transfer the acetonitrile phases to a 1-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for about 30 sec. Extract with two 100-ml portions of hexane by vigorously shaking about 15 sec.

9.3.2.6.3 Combine the hexane extracts in a 1-liter separatory funnel and wash with two 100-ml portions of distilled water. Discard the water layer and pour the hexane layer through a 8-10 cm anhydrous sodium sulfate column into a 500-ml Kuderna-Danish flask equipped with a 10-ml ampul. Rinse the separatory funnel and column with three 10-ml portions of hexane.

9.3.2.6.4 Concentrate the extracts to an appropriate volume.

9.3.2.6.5 Analyze as described in Section 10.0.

9.3.2.7 Florisil slurry cleanup

9.3.2.7.1 Place the sample extract into a 20-ml narrow-mouth screw-cap container. Add 0.25 g of Florisil (PR grade or equivalent). Seal with a Teflon-lined screw cap and shake for 1 min.

9.3.2.7.2 Allow the Florisil to settle; then decant the treated solution into a second container with rinsing. Concentrate the sample to an appropriate volume. Analyze as described in Section 10.0.

9.3.2.8 Base cleanup[6]

9.3.2.8.1 Quantitatively transfer the concentrated extract to a 125-ml extraction flask with the aid of several small portions of solvent.

9.3.2.8.2 Evaporate the extract just to dryness with a gentle stream of dry filtered nitrogen, and add 25 ml of 2.5% alcoholic KOH.

9.3.2.8.3 Add a boiling chip, put a water condenser in place, and allow the solution to reflux on a hot plate for 45 min.

9.8.2.8.4 After cooling, transfer the solution to a 250-ml separatory funnel with 25 ml of distilled water.

9.3.2.8.5 Rinse the extraction flask with 25 ml of hexane and add it to the separatory funnel.

9.3.2.8.6 Stopper the separatory funnel and shake vigorously for at least 1 min. Allow the layers to separate and transfer the lower aqueous phase to a second separatory funnel.

9.3.2.8.7 Extract the saponification solution with a second 25-ml portion of hexane. After the layers have separated, add the first hexane extract to the second separatory funnel and transfer the aqueous alcohol layer to the original separatory funnel.

9.3.2.8.8 Repeat the extraction with a third 25-ml portion of hexane. Discard the saponification solution, and combine the hexane extracts.

9.3.2.8.9 Concentrate the hexane layer to an appropriate volume and analyze according to Section 10.0.

10.0 Gas Chromatographic/Electron Impact Mass Spectrometric Determination

10.1 Internal standard addition - An appropriate volume of the internal standard solution is pipetted into the sample. The final concentration of the internal standard must be in the working range of the calibration and well above the matrix background. The internal standard is thoroughly incorporated by mechanical agitation.

Note: The volumetric measurement of the internal standard solution is critical to the overall method precision. The analyst must exercise caution that the volume is known to be ±1% or better. Where necessary, calibration of the pipet is recommended.

10.2 Tables 2, and 5 through 8 summarize the recommended operating conditions for analysis. Figure 1 presents an example of a chromatogram.

10.3 While the highest available chromatographic resolution is not a necessary objective of this protocol, good chromatographic performance is recommended. With the high resolution of CGC, the probability that the chromatographic peaks consist of single compounds is higher than with PGC. Thus, qualitative and quantitative data reduction should be more reliable.

10.4 After performance of the system has been certified for the day and all instrument conditions set according to Tables 2, and 5 through 8, inject an aliquot of the sample onto the GC column. If the response for any ion, including surrogates and internal standards, exceeds the working range of the system, dilute the sample and reanalyze. If the responses of surrogates, analyte, or internal standard are below the working range, recheck the system performance. If necessary, concentrate the sample and reanalyze.

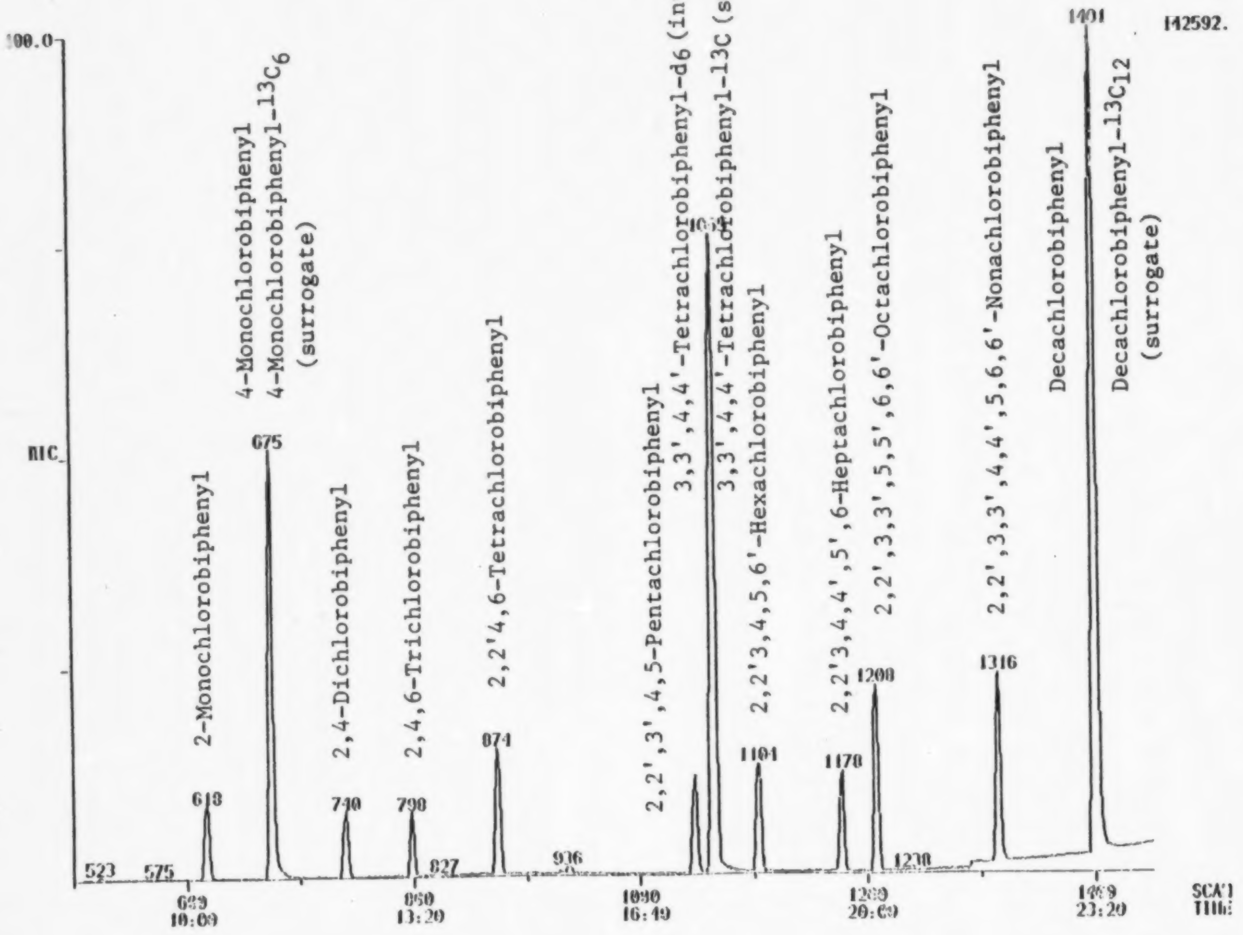

Figure 1. Capillary gas chromatography/electron impact ionization mass spectrometry (CGC/EIMS) chromatogram or the calibration standard solution required for quantitation of PCBs by homolog. This chromatogram includes PCBs representative of each homolog, three carbon-13 labeled surrogates, and the deuterated internal standard. The concentration of all components and the CGC/EIMS parameters are presented in Tables 3, 4, 5, and 7.

10.5 Record all data on a digital storage device (magnetic disk, tape, etc.) for qualitative and quantitative data reduction as discussed below.

11.0 Qualitative Identification

11.1 Selected ion monitoring (SIM) or limited mass scan (LMS) data - The identification of a compound as a given PCB homolog requires that two criteria be met:

11.1.1 (1) The peak must elute within the retention time window set for that homolog (Section 7.5); and (2) the ratio of two ions obtained by SIM (Table 11) or by LMS (Table 12) must match the natural ratio within ±20%. The analyst must search the higher mass windows, in particular M+70, to prevent misidentification of a PCB fragment ion cluster as the parent.

11.1.2 If one or the other of these criteria is not met, interferences may have affected the results and a reanalysis using full scan EIMS conditions is recommended.

11.2 Full scan data

11.2.1 The peak must elute within the retention time windows set for that homolog (as described in Section 7.5).

11.2.2 The unknown spectrum must match that of an authentic PCB. The intensity of the three largest ions in the molecular cluster (two largest for monochlorobiphenyls) must match the natural ratio within ±20%. Fragment clusters with proper intensity ratios must also be present.

11.2.3 Alternatively, a spectral search may be used to automatically reduce the data. The criteria for acceptable identification include a high index of similarity. For the Incos 2300, a fit of 750 or greater must be obtained.

11.3 Disputes in interpretation - Where there is reasonable doubt as to the identity of a peak as a PCB, the analyst must either identify the peak as a PCB or proceed to a confirmational analysis (see Section 13.0).

12.0 Quantitative Data Reduction

12.1 Once a chromatographic peak has been identified as a PCB, the compound is quantitated based either on the integrated abundance of the SIM data or EICP for the primary characteristic ion in Tables 11 and 12. If interferences are observed for the primary ion,

TABLE 11. CHARACTERISTIC SIM IONS FOR PCBs

Homolog	Ion (relative intensity)		
	Primary	Secondary	Tertiary
$C_{12}H_9Cl$	188 (100)	190 (33)	-
$C_{12}H_8Cl_2$	222 (100)	224 (66)	226 (11)
$C_{12}H_7Cl_3$	256 (100)	258 (99)	260 (33)
$C_{12}H_6Cl_4$	292 (100)	290 (76)	294 (49)
$C_{12}H_5Cl_5$	326 (100)	328 (66)	324 (61)
$C_{12}H_4Cl_6$	360 (100)	362 (82)	364 (36)
$C_{12}H_3Cl_7$	394 (100)	396 (98)	398 (54)
$C_{12}H_2Cl_8$	430 (100)	432 (66)	428 (87)
$C_{12}HCl_9$	464 (100)	466 (76)	462 (76)
$C_{12}Cl_{10}$	498 (100)	500 (87)	496 (68)

Source: Rote, J. W., and W. J. Morris, "Use of Isotopic Abundance Ratios in Identification of Polychlorinated Biphenyls by Mass Spectrometry," J. Assoc. Offic. Anal. Chem., 56(1), 188-199 (1973).

TABLE 12. LIMITED MASS SCANNING (LMS) RANGES FOR PCBs

Compound	Mass range (m/z)[a]
$C_{12}H_9Cl_1$	186-190
$C_{12}H_8Cl_2$	220-226
$C_{12}H_7Cl_3$	254-260
$C_{12}H_6Cl_3$	288-294
$C_{12}H_5Cl_5$	322-328
$C_{12}H_4Cl_6$	356-364
$C_{12}H_3Cl_7$	386-400
$C_{12}H_2Cl_8$	426-434
$C_{12}HCl_9$	460-468
$C_{12}Cl_{10}$	494-504
$C_{12}D_6Cl_4$	294-300
$^{13}C_6{}^{12}C_6H_9Cl$	192-196
$^{13}C_{12}H_6Cl_4$	300-306
$^{13}C_{12}H_2Cl_8$	438-446
$^{13}C_{12}Cl_{10}$	506-516

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[a] Adapted from Tindall, G. W., and P. E. Wininger, "Gas Chromatography-Mass Spectrometry Method for Identifying and Determining Polychlorinated Biphenyls," J. Chromatogr., 196, 109-119 (1980).

use the secondary and then tertiary ion for quantitation. If interferences in the parent cluster prevent quantitation, an ion from a fragment cluster (e.g., M-70) may be used. Whichever ion is used, the RF must be determined using that ion. The same criteria should be applied to the surrogate compounds (Table 13).

12.2 Using the appropriate analyte-internal standard pair and response factor (RF_p) as determined in Section 7.3, calculate the concentration of each peak using Equation 12-1.

$$\text{Concentration } (\mu g/g) = \frac{A_p}{A_{is}} \cdot \frac{1}{RF_p} \cdot \frac{M_{is}}{M_e} \cdot \frac{V_e}{V_i} \qquad \text{Eq. 12-1}$$

where A_p = area of the characteristic ion for the analyte PCB peak

A_{is} = area of the characteristic ion for the internal standard peak

RF_p = response factor of a given PCB congener

M_{is} = mass of internal standard injected (micrograms)

M_e = mass of sample extracted (grams)

V_i = volume injected (microliters)

V_e = volume of sample extract (microliters)

12.3 If a peak appears to contain non-PCB interferences which cannot be circumvented by a secondary or tertiary ion, either:

12.3.1 Reanalyze the sample on a different column which separates the PCB and interferents;

12.3.2 Perform additional chemical cleanup (Section 9) and then reanalyze the sample; or

12.3.3 Quantitate the entire peak as PCB.

12.4 Calculate the recovery of the four ^{13}C surrogates using the appropriate surrogate-internal standard pair and response factor (RF_{is}) as determined in Section 7.4 using Equation 12-2.

$$\text{Recovery } (\%) = \frac{A_s}{A_{is}} \cdot \frac{1}{RF_s} \cdot \frac{M_{is}}{M_s} \cdot 100 \qquad \text{Eq. 12-2}$$

where A_s = area of the characteristic ion for the surrogate peak

A_{is} = area of the characteristic ion for the internal standard peak

TABLE 13. CHARACTERISTIC IONS FOR ^{13}C-LABELED PCB SURROGATES

Specific compound	Ion (relative intensity)		
	Primary	Secondary	Tertiary
$^{13}C_6{}^{12}C_6H_9Cl$	194 (100)	196 (33)	-
$^{13}C_{12}H_6Cl_4$	304 (100)	306 (49)	302 (78)
$^{13}C_{12}H_2Cl_8$	442 (100)	444 (65)	440 (89)
$^{13}C_{12}Cl_{10}$	510 (100)	512 (87)	514 (50)

RF_s = response factor for the surrogate compound with respect to the internal standard (Equation 7-2)

M_{is} = mass of internal standard injected (nanograms)

M_s = mass of surrogate, assuming 100% recovery (nanograms)

12.5 Correct the concentration of each peak using Equation 12-3. This is the final reportable concentration.

$$\text{Corrected concentration } (\mu g/g) = \frac{\text{Concentration } \mu g/g}{\text{Recovery } (\%)} \cdot 100 \qquad \text{Eq. 12-3}$$

12.6 Sum all of the peaks for each homolog, and then sum those to yield the total PCB concentration in the sample. Report all numbers in µg/g. The reporting form in Table 14 may be used. If an alternate reporting format (e.g., concentration per peak) is desired, a different report form may be used. The uncorrected concentrations, percent recovery, and corrected recovery are to be reported.

12.7 Round off all numbers reported to two significant figures.

13.0 Confirmation

If there is reason to question the qualitative identification (Section 11.0), the analyst may choose to confirm that a peak is not a PCB. Any technique may be chosen provided that it is validated as having equivalent or superior selectivity and sensitivity to GC/EIMS. Some candidate techniques include alternate GC columns (with EIMS detection), GC/CIMS, GC/NCIMS, high resolution EIMS, and MS/MS techniques. Each laboratory must validate confirmation techniques to show equivalent or superior selectivity between PCBs and interferences and sensitivity (limit of quantitation, LOQ).

If a peak is confirmed as being a non-PCB, it may be deleted from the calculation (Section 12). If a peak is confirmed as containing both PCB and non-PCB components, it must be quantitated according to Section 12.3.

14.0 Quality Control

14.1 Each laboratory that uses this method must operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory must maintain performance records to define the quality of data that are generated. After a date specified by the Agency, ongoing performance checks should be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

TABLE 14. ANALYSIS REPORT

INCIDENTAL PCBs IN WASTEWATER

Sample No. ______________________
Sample Matrix ____________________
Sample Source ____________________
Notebook No. or File Location ________

Volume Extracted ____________ liter
Extraction/Cleanup Procedure ____

Int. Std.	Mass Added (μg)	(Circle one)		Ratio	Intensity
4-Cl(d_6)		298	300	100/49	

Surrogates	Mass Added (μg)	(Circle one)		Ratio	Intensity	% Recovery
1-Cl		194	196	100/33		
4-Cl		304	306	100/49		
8-Cl		442	444	100/65		
10-Cl		510	512	100/87		

(continued)

TABLE 14 (continued)

			Qualitative					Quantitative			
Analyte	1°	2°	I_{1°	I_{2°	Ratio	Theoretical	OK?	Ion Used	RF	Uncorr Conc. (µg/ℓ)	Corr Conc (µg/ℓ)
1-Cl	188	190				100/33					
2-Cl	222	224				100/66					
3-Cl	256	258				100/99					
4-Cl	292	290				100/76					
5-Cl	326	328				100/66					
6-Cl	360	362				100/82					
7-Cl	394	396				100/98					
8-Cl	430	432				100/66					
9-Cl	464	466				100/76					
10-Cl	498	500				100/87					
Total										µg/ℓ Uncorr.	µg/ℓ Corr.

Reported by:	Internal Audit:	EPA Audit:
Name	Name	Name
Signature/Date	Signature/Date	Signature/Date
Organization	Organization	Organization

14.2 The analysts must certify that the precision and accuracy of the analytical results are acceptable by:

14.2.1 The absolute precision of surrogate recovery, measured as the RSD_s of the integrated EIMS area (A_s) for a set of samples, must be ±10%.

14.2.2 The mean recovery (R_c) of at least four replicates of a QC check sample to be supplied by the Agency must meet Agency-specified accuracy and precision criteria. This forms the initial data base for establishing control limits (see Section 14.3 below).

14.3 Control limits - The laboratory must establish control limits using the following equations:

$$\text{Upper control limit (UCL)} = R_c + 3\ RSD_c$$

$$\text{Upper warning limit (UWL)} = R_c + 2\ RSD_c$$

$$\text{Lower warning limit (LWL)} = R_c - 2\ RSD_c$$

$$\text{Lower control limit (LCL)} = R_c - 3\ RSD_c$$

These may be plotted on control charts. If an analysis of a check sample falls outside the warning limits, the analyst should be alerted that potential problems may need correction. If the results for a check sample fall outside the control limits, the laboratory must take corrective action and recertify the performance (Section 14.2) before proceeding with analyses. The warning and control limits should be continuously updated as more check sample replicates are added to the data base.

14.4 Before processing any samples, the analyst should demonstrate through the analysis of a reagent blank that all glassware and reagent interferences are under control. Each time a set of samples is analyzed or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against contamination.

14.5 Procedural QC - The various steps of the analytical procedure should have quality control measures. These include but are not limited to:

14.5.1 GC performance - See Section 7.1 for performance criteria.

14.5.2 MS performance - See Section 7.2 for performance criteria.

14.5.3 Qualitative identification - At least 10% of the PCB identifications, as well as any questionable results, should be confirmed by a second mass spectrometrist.

14.5.4 Quantitation - At least 10% of all manual calculations, including peak area calculations, must be checked. After changes in computer quantitation routines, the results should be manually checked.

14.6 A minimum of 10% of all samples, one sample per month or one sample per matrix type, whichever is greater, selected at random, must be run in triplicate to monitor the precision of the analysis. An RSD of ±30% or less must be achieved. If the precision is greater than ±30%, the analyst must be recertified (see Section 14.2).

14.7 A minimum of 10% of all samples, one sample per month or one sample per matrix type, whichever is greater, selected at random, must be analyzed by the standard addition technique. Two aliquots of the sample are analyzed, one "as is" and one spiked (surrogate spiking and equilibration techniques are described in Section 9.2) with a sufficient amount of Solution CSxxx to yield approximately 100 µg/liter of each compound). The samples are analyzed together and the quantitative results calculated. The recovery of the spiked compounds (calculated by difference) must be 80-120%. If the sample is known to contain specific PCB isomers, these isomers may be substituted for solution CSxxx. If the concentrations of PCBs are known to be high or low, the amount added should be adjusted so that the spiking level is 1.5 to 4 times the measured PCB level in the unspiked sample.

14.8 Interlaboratory comparison - Interlaboratory comparison studies are planned. Participation requirements, level of performance, and the identity of the coordinating laboratory will be presented in later revisions.

14.9 It is recommended that the participating laboratory adopt additional QC practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates or triplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

15.0 Quality Assurance

Each participating laboratory must develop a quality assurance plan according to EPA guidelines.[7] The quality assurance plan must be submitted to the Agency for approval.

16.0 Method Performance

The method performance is being evaluated. Limits of quantitation; average intralaboratory recoveries, precision, and accuracy; and interlaboratory recoveries, precision, and accuracy will be presented.

17.0 Documentation and Records

Each laboratory is responsible for maintaining full records of the analysis. Laboratory notebooks should be used for handwritten records. GC/MS data must be archived on magnetic tape, disk, or a similar device. Hard copy printouts may be kept in addition if desired. QC records should be maintained separately from sample analysis records.

The documentation must describe completely how the analysis was performed. Any variances from the protocol must be noted and fully described. Where the protocol lists options (e.g., sample cleanup), the option used and specifics (solvent volumes, digestion times, etc.) must be stated.

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